Some Factors Affecting the Accuracy of the Flame Spectrophotometric Determination of Magnesium in Soils

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INTRODUCTION

Magnesium is one of the four major cations that are essential to plant growth. It is the one needed in the smallest quantity and, comparatively speaking, has received far less attention than any of the four.

The study of magnesium and its interactions in the soil has been going on at an increasing rate for the last thirty years. Prior to this time, very little fertilizer was applied to the soil, hence yields were not so large and the tax on soil magnesium was not great. In the early days of fertilizer use, low analysis fertilizers had dolomite incorporated as a filler. This filler was thought to be inert as far as fertilizer materials were concerned; however the magnesium that was contained in the filler of these fertilizers was sufficient to prevent the appearance of magnesium deficiency symptoms, especially where low rates of fertilizers were applied and relatively low yields were common.

Since the advent of high analysis fertilizers, where the quantity of dolomite used as a filler is reduced or left out completely, more stress is placed on the reserve of magnesium in the soil. This is especially true where high

rates of fertilizer are used and the soil supply of magnesium is low.

The failure to incorporate magnesium containing materials in fertilizer is not the only reason why magnesium limits plant growth. Warm climates, high rainfall and sandy soils are very conducive to magnesium loss by leaching. Of all the cations, magnesium is exceeded only by sodium and calcium in relative rate of leaching from the soil. This problem is particularly important in areas low in native magnesium.

During the past several years the appearance of magnesium deficiency symptoms have been noticed throughout the entire Peninsular of Florida. The areas where light sandy soils predominate are the ones where the deficiencies are the most severe. Crops growing on the heavier soils of west Florida have also shown magnesium deficiency symptoms.

The importance of this problem is emphasized by a survey conducted by the soil testing laboratory at the University of Florida. The analyses of over eight thousand soil samples sent to the laboratory from 62 Florida counties indicate that in 55 per cent of these soil samples the available magnesium is low enough to be a limiting factor for plant growth.

The three main areas in the state where available magnesium is lowest and is known to be causing trouble are;

the Suwannee Valley area, the ridge section, and most of west Florida. The areas not mentioned are certainly not without soils deficient in magnesium; however, in the above mentioned areas the problem appears to be most severe.

Magnesium, although essential to plant growth, has not generally been included in a soil test program because of the difficulties encountered in previous methods of analysis.

The experiments reported in this thesis were conducted in the Soils Department of the University of Florida's Agricultural Experiment Station. The objectives of this work were two fold. First to determine what ions, present in either plants or soils, cause errors in the flame spectrophotometric determination of magnesium using the oxy-hydrogen flame and a photomultiplier attachment. Three wavelengths were studied to determine which wavelength would be most free of interferences. Methods of eliminating the ions that were found to interfere were also studied. The second objective was to study magnesium levels in soils in the greenhouse and in field experiments with respect to the interactions with other ions and to determine the rate and frequency at which magnesium should be applied.

REVIEW OF LITERATURE

Magnesium Deficiency

The symptoms of magnesium deficiency are definite and easily recognized. When the plant is unable to absorb magnesium in sufficient quantities, it is shown first in the chlorophyll of the older leaves. A yellow streaking develops between the veins. Dark green blotches appear in chain like fashion along these veins. The yellow areas may become white or even dead areas depending upon the extent of the deficiency.

Eisenmenger and Kucinski (53) found that families of seed plants in the lower stages of evolutionary development always had high magnesium requirements. The highly developed plants, except corn, potatoes, and cucurbita, did not show magnesium deficiency symptoms.

Lutman and Waldbridge (90) theorized on the "exhaustion of organs", maintaining that the withdrawal of magnesium from older leaves resulted in the destruction of chlorophyll, and led to yellowing, premature ageing, and eventual death of the plant. The role of magnesium is probably secondary in senescence. The lack of magnesium

along with other complicated internal disturbances are probably responsible for normal ageing.

Magnesium deficiency results not only in chlorophyll loss, but also of xanthophyll and carotene loss. This loss, regardless of liming, was in a constant ratio of 20:2:1, respectively (73). According to Garner (61) magnesium deficient leaves contained less carbohydrates than leaves adequately supplied with this element.

A deficiency of magnesium in plants is caused by a low supply of magnesium in the soil, low solubility, leaching, insufficient rate of absorption due to selective absorption of cations of higher activities, such as potassium, calcium, sodium, and ammonia.

Magnesium deficiencies have been reported mostly on the more sandy soils; however, Davis (46) reports a magnesium deficiency in celery growing on organic soils in Michigan.

Leaf scorch of apple, a magnesium deficiency symptom, was reported in Maine by Chucka (40).

Greenhouse tomatoes in New Zealand are commonly seen with magnesium deficiency (98). The chlorosis characteristic of magnesium deficiency is also associated with a higher concentration of potash in the leaves, (27, 33, 94, 154).

Blue (20) reported severe deficiencies of sweet clover, millet, and oats under intensive fertilization in the Suwannee Valley area. Magnesium values as low as 20 ppm were reported, in the upper six inches of the soil.

Physiological Functions of Magnesium in Plants

Magnesium is the only mineral constituent found in the chlorophyll molecule. In 1893, Schreiber (140) found by the physiological analysis of plants growing on certain soils that these soils were low in magnesium. Other work by this author confirmed his belief that magnesium was necessary in the formation of chlorophyll.

Zimmerman (179) writes that magnesium comprises 27 per cent of the chlorophyll molecule. Magnesium deficiency affects chlorophyll formation and indirectly photosynthesis. Rabinowitch (128) states that as magnesium becomes more deficient, the rate of photosynthesis is reduced accordingly. Much more magnesium was necessary to bring about full rate of photosynthesis than was necessary to prevent a deficiency.

Chlorophyll magnesium, according to Javillier and Goudshaux (79) represents only about 10 to 30 milligrams per 100 grams of dry leaves in 22 plant species. The ratio of chlorophyll magnesium to total leaf magnesium was from 0.8 to 26 in nine different plants. Willstatter (176) found the average content of chlorophyll in green leaves to be about 0.8 per cent of the dry weight and that magnesium moved within the plant quite readily.

Serono et al. (142) in 1951 synthesized formaldehyde in vitro from carbon dioxide and water through the action of infrared rays in the presence of magnesium. They

attempted to prove experimentally that magnesium in chlorophyll acts as a catalyst in the formation of formaldehyde which is immediately used up in the formation of carbohydrates.

Finkle and Appleman (55) found that magnesium is required for the production of both the metal-porphyrins, catalase and chlorophyll.

By theorizing that magnesium acts as a carrier of phosphates, Loew (86) found that magnesium was closely related to phospholipid formation and to the synthesis of nucleoproteins in plant cells. To add to the importance of this theory is the fact that magnesium was found to be abundant in meristematic cells.

Most of the magnesium is found in the chlorophyll bearing part of the plant although seeds are relatively rich in magnesium. In the role as a carrier of phosphates, magnesium functions indirectly in nucleic acid production. Oily seeds which are high in magnesium are also high in phosphate rich lecithin. Magnesium was found more abundantly in oily seeds than in non-oily seeds.

According to Pfutzer *et al.* (121), phosphorus is responsible for increases in vitamin B_1 in plants. Magnesium is directly related to phosphate uptake from the soil by plants and phosphorus translocation in the plant so it is indirectly related to vitamin synthesis. Following the

same line of reasoning that magnesium exhibits on the uptake of potassium and knowing that potassium influences vastly the formation of ascorbic acid it follows that magnesium is again indirectly related to this important function.

Lecat (85) also concluded that increased magnesium fertilization, along with potash, increased the production of chemically reduced ascorbic acid in plant tissue. A deficiency of magnesium and/or potash causes an abnormal accumulation of ascorbic acid in leaves.

Raumer (129) was first to suggest that magnesium was involved in the transfer of starch from leaves to stems. He later suggested that there was a relationship between magnesium and carbohydrate transfer within plants.

Another very important function of magnesium is that of activating the enzyme hexokinase. Saltman (136) stated that manganese is about 80 per cent as effective as magnesium in activating this enzyme. Hexokinase is essential in the phosphorylation of glucose, mannose, fructose, and glucosamine.

Steffensen (151) attributed sticky chromosomes and chromosome aberrations to magnesium deficiency and related it to the metabolism of desoxyribose nucleic acid metabolism.

Plant Requirements for Magnesium

The amount of magnesium contained in most plants usually ranks either third or fourth of the metallic ions. In the more humid regions, where sodium concentration is low, magnesium ranks third.

Garner et al. (61) found that the total magnesium content of the leaf must be several times the quantity present in chlorophyll in order to prevent breakdown of chlorophyll.

Plant requirements for magnesium vary with families. According to Collander (42) Chenopodiacea and Fagopyrum families are always rich in magnesium. Pisum vicia and Avena are relatively poor in this element.

Beeson (14) compiled quite an extensive summarization of the average mineral composition of all types of plants at various stages of growth. The average magnesium content of 19 different grass species was 0.156 per cent.

Daniel (45) reported the average magnesium concentration of six species of mature legumes was 0.379 per cent. From the above data it may be inferred that the magnesium requirement of legumes is about two and one-half times more than for non-legumes. Bender and Eisenmenger (16) were in agreement with this.

Newton (111) offered an explanation as to why legumes had higher magnesium concentrations than non-legumes. He stated that roots of legumes give off more CO_2 than non-

legumes. This CO_2 increases the solubility of calcium and magnesium compounds and the roots pick them up.

The growth of plants is more severely retarded by the absence of magnesium early in their life than later on (166).

Rapid-growing plants such as potatoes, cabbage, spinach, cucumbers, and corn have definite periods in their growth during which their magnesium requirement is very high. Carolus and Brown (37) stated, that if magnesium is not present in abundance at this time a deficiency will occur in the lower foliage.

Peterson and Berger (120) found that the addition of 50 ppm of magnesium to the nutrient solution caused peas to bloom three to seven days before the ones receiving only 5 ppm. They also reported that seed germination was 100 per cent on the 50 ppm magnesium treated seed and 42 per cent on the 5 ppm magnesium treated seed.

Cereals thrive best when the calcium content slightly exceeds the magnesium content (86, 176). Lowe (86) reported that cabbage required twice as much calcium as magnesium and buckwheat three times as much.

Willstatter (176) found that the magnesium content of the seed frequently exceeded that of its pod. The nutritative tissues of the seed frequently contain more magnesium than the green assimilating parts of the plant.

Magnesium is concentrated mainly in the stalks in the corn plant, the percentage in the stover being about three times the concentration in the grain. The magnesium added to soil was found present in greater concentrations in vegetative organs than in seed (155).

Cohn and Bougy (41) found that magnesium requirement of sugar beets was much greater than for the edible variety of beets. At the early stage of growth the requirement was the same; however, as the sugar began to accumulate the magnesium difference became evident.

Riggs (133) found the distribution of magnesium in the older leaves of a pine leader to contain about one-half as much magnesium as the young tip leaves.

The potato plant absorbed seven per cent of its total magnesium during the first 50 days of growth, 60 per cent the next 30 days, and the remaining 33 per cent the last 30 days. During the first two periods the percentage of magnesium absorbed was lower than that for calcium or potassium; however, during the third period the percentage of magnesium absorbed was greater (70).

Hester (71) reported that in tomatoes the absorption of magnesium was three per cent during the first month, 20 per cent during the second, and 77 per cent during the last month. Calcium and potassium absorption was greater during the second month.

During maturation of the soybean plant, Borst and Thatcher (24) reported that the magnesium content of the stem decreased as well as other cations and phosphorus. Magnesium in the leaves remained fairly constant.

Hashimoto and Okamoto (68, 69) found that soybean plants required more magnesium during pod formation. Magnesium was considered necessary for the development of pectin in the middle lamella of cells.

The translocation of magnesium from older leaves to newly developing leaves was not nearly so great as the translocation to the fruit, according to Reed and Haas (130). Along this same line and bearing out the above conclusions is the work of Fudge (58). He found that magnesium deficiency in citrus was associated with seedy varieties. Leaves dropped from trees of the seedy varieties showing magnesium deficiencies when seedless varieties growing on the same soil showed no visible deficiency symptoms. He stated that the magnesium requirement for citrus is equal to the phosphorus requirement.

Blanchet (19) observed that the deficiency of magnesium in apple trees reduced the wood growth more than it affected yield.

Moone et al. (106) reported that leaf scorch resulted in apple leaves when magnesium moved from the leaves and to the seed during fruiting.

It is suggested by Cooper et al. (44) that a relatively high content of magnesium and phosphorus in seed indicates that magnesium may be the strongest cation that could be utilized in combination with phosphorus and give sufficient assimilation of phosphorus in the seed for normal growth of seedling plants. This is very closely in line with the energy that is available from the sun for ready assimilation of magnesium hydrogen phosphate as compared to the stable calcium hydrogen phosphate that would require more energy than is actually available.

Soil Magnesium

It has been pointed out by several authors (36, 44, 63) that magnesium is probably limiting plant growth on many soils. The yields of most plants deficient in magnesium are reduced before any visible symptoms of magnesium deficiency occur.

When a plant shows a deficiency in magnesium it means that the plant is unable to absorb magnesium from the soil on which it is growing at a rate equal to the plant requirement for this element. There are several reasons why this may occur. The soil reserve may have been depleted by leaching and crop removal to the point where there is not enough magnesium for maximum yield. The magnesium may be in a form that is insoluble or soluble at such a low rate that

it is inadequate for optimum plant growth. Other ions may be present in sufficient quantities to suppress the absorption of magnesium by plants.

The importance of proper cation and anion balance to magnesium absorption has been pointed out (13, 15, 77, 114, 158, 166). Zimmerman (180) stated that at a low soil fertility level, magnesium uptake is related mainly to that available in the soil; however, at higher levels of fertility the cationic ratios play an important part.

Southwick (149) questioned the use of potassium compounds in the fertilization of apple orchards until the magnesium level was built up. On Florida soils, Spencer (150) concluded that magnesium and potassium should be applied separately and at different times during the year.

Mehlich (100) added calcium, magnesium, and potassium in an exchangeable form to a soil colloid. When the calcium to magnesium and calcium to potassium ratios were four, the calcium to magnesium ratios in wheat were four and in alfalfa eight. The calcium to potash ratios in wheat roots were ten and in alfalfa roots twenty-four.

McLean (96) using very small concentrations of potassium reduced the activity of magnesium to a very low degree in montmorillonite. Much higher concentrations of potassium were required to drop the magnesium activity to the same point in beidellite and halloysite clays (101).

MacGregor and Rost (91) reported that plants growing on soils naturally high in calcium and magnesium carbonates did not respond any differently with regard to potassium uptake than ones on low carbonate soils; however, calcium and magnesium uptake was greatest on the high carbonate soils.

The loss of magnesium and calcium from the soil is greatest at low soil reactions according to Jamison (78). Soil pH is a factor in potash retention in Florida soils, although it is of little consequence, he stated.

Boynton and Embleton (29) found that in soils high in replaceable magnesium, the magnesium to potassium ratio may determine the availability of magnesium, particularly with decreasing calcium saturation.

According to the findings of Mulder (109), the lower the pH of the soil the lower is the amount of absorbable magnesium in the soil and the ability of the plant to absorb magnesium is lower because of a limited root system.

Bear et al. (11) found that New Jersey soils ran from 0.02 per cent to more than 1.0 per cent magnesium. He stated that a magnesium deficiency is likely to develop when the magnesium portion of the exchange complex falls below six per cent or when the potassium to magnesium ratio of the exchange complex exceeds 1:2. Soils, where the magnesium saturation exceeds thirty per cent, exhibit properties of an alkaline soil. These soils have a magnesium to potassium

ratio of 10 or 15 to one. This poor situation was corrected by the addition of one thousand pounds of potassium per acre initially and two hundred pounds per acre annually thereafter.

Prince et al. (127) found that crops, growing on soils where the magnesium concentration is less than six per cent of the exchange cations will respond to added magnesium.

Magnesium and calcium may become deficient on alkali soils that are high in sodium according to Bower and Turk (25). They concluded that calcium and magnesium react with the high amounts of carbonate and bicarbonate ions to form insoluble calcium and magnesium carbonates of very low availability. This might also be explained by the relative ionic strenghts of the elements in plant absorption reported by Wilson (177). Potassium is more active than sodium, sodium is more active than calcium, and calcium is more active than magnesium.

Pope and Munger (124) reported several varieties of plants growing on muck soil showed severe symptoms of magnesium deficiency while another variety nearby had no symptoms. He found that one single gene was responsible for conditioning the utilization of magnesium.

Prince (126) recommended annual applications of forty pounds of magnesium per acre on New Jersey soils. Part of this magnesium should be applied as a side dressing late in the growing season.

Leaching of Magnesium

The leaching of magnesium is very pronounced in sandy soils where rainfall is heavy. Using large lysimeters, Volk (162) found that magnesium equivalent to one-third of the 50 pounds per acre of magnesium sulfate added to a Norfolk loamy fine sand was leached during a five-month period from February to July. He reported only a slight difference in the leaching of calcium and magnesium due to the additions of chloride, nitrate, or sulfate ions. Band placement resulted in a marked increase in movement of magnesium as compared to broadcast applications.

MacIntire, et al. (92) found that the magnesium loss due to ammonium chloride was greatest the second year. The loss due to ammonium sulfate was greatest during the second and third years and the loss due to ammonium phosphate was greatest in the third year. Outgo of magnesium, as the chloride was twice the outgo induced by phosphate and 1.4 times that induced by sulfate. Calcium exchange was twice the magnesium exchange.

Lott (89) reported about 80 per cent of the magnesium applied as magnesium sulfate was lost during the first year.

The loss of calcium and magnesium by leaching was increased due to the application of ammonium sulfate as a fertilizer and sulfur as a dust in insect control. This

was accompanied by a pH decline to about 4.0, according to Boynton (26).

Boynton and Embleton (29) concluded that the ease of leaching of calcium and magnesium along with the low leaching of potash is conducive to magnesium deficiency.

Magnesium as a Fertilizer Element

The yield of several agronomic and horticultural plants have been increased significantly by the addition of magnesium to the soil (11, 50, 97, 120, 148, 160).

In 1922 Garner (63) was the first to report the use of magnesium as an element for practical fertilizer usage. In the past, when dolomite was used as a filler in low analysis fertilizers, much of the credit that went to potash was probably due to the magnesium contained in the mixture as pointed out by Camp (34).

Cooper *et al.* (44) concluded that in humid climates the magnesium content of plants is exceeded only by potassium and calcium. The fact that magnesium is so easily leached suggests that it may logically be the next metallic element that should be incorporated in mixed fertilizers. This is especially true where high analysis fertilizers are used and high yields are expected.

The use of high analysis fertilizers has resulted in a lowering of the pH, an increase in exchangeable hydrogen,

and a decrease in exchangeable calcium and magnesium (10).

Fast growing crops such as potatoes, cotton, tobacco, tomatoes, and other vegetables have often given a marked response to magnesium applied as a fertilizer (7, 15, 42).

Longstaff and Graham (88) have listed the order of availabilities of several magnesium sources that could be used in mixed fertilizers. In decreasing order of availability they are: dolomite, magnesite, olivine, talc, and hornblend. Magnesium sulfate is the most soluble source and the one most used.

Sulfate of potash magnesia has been used as a fertilizer for many years and finds extensive use as a side dressing to many crops. Kalinkevich (83) reported that sulfate of potash magnesia increased the protein content of clover 100 per cent over the same amount of potassium applied as muriate of potash. He attributed this difference to the presence of magnesium; however, he failed to consider the sulfur. If sulfur was deficient, part of the response may have been due to this element.

In 1951 a new fertilizer material, magnesium phosphate was introduced on the fertilizer market. Schatzel (139) reported that it contained 18-22 per cent P_2O_5, 12-14 per cent MgO, 26-28 per cent CaO, and 28-30 per cent sulfate. The fertilizer value is equal to that of superphosphate.

Both olivine and dolomite have proven to be good available sources of magnesium for citrus, as measured by growth, yield, and concentration of magnesium in the plant. Nine tons of dolomite produced less growth than one ton; however, the nine ton rate of olivine produced the largest dry weight yield (153).

The application of dolomite to soils to supplement the soil supply of available magnesium and to increase yield has been very successful in the past few years (12, 21, 29, 40, 44, 117, 161).

Cooper et al.(44) found that a broadcast application of dolomite would supply the magnesium required for plant growth for years.

Dolomite limestone was found to be sufficiently soluble at a soil pH below 5.7 to increase the pH as well as supply available magnesium, Peech (117).

Beckenbach (12) concluded that soils deficient in both calcium and magnesium should be limed with dolomite. On soils high in calcium, but deficient in magnesium, magnesium sulfate should be added.

The leaf content of apples was increased 100 per cent by the application of dolomite to the soil according to Boynton and Embleton (29).

Magnesium deficiency symptoms on various crops were easily corrected by spraying a solution of magnesium

sulfate on the leaves (40, 46, 72), and by soil applications of magnesium sulfate (20, 40, 44, 46, 72, 103, 131, 154, 156, and 171).

Hill and Johnston (72) reported that the full response to magnesium applied as magnesium sulfate may be delayed two or three years. Nickelsen (103) reports that blueberries respond to 300 pounds of magnesium sulfate the following year.

Reitz and Long (131) did not obtain any response to 13.5 pounds per tree of magnesium oxide applied as magnesium sulfate after five years. The fate of applied magnesium sulfate and why it was not picked up by plants was questioned.

Interactions of the Magnesium Ion with Other Ions

Magnesium and Phosphorus Interactions.--In 1903 Loew (86) postulated that the role of magnesium, in addition to being a part of chlorophyll, is that of a carrier of phosphates within the plants. He also believed that magnesium was related to phospholipid formation.

A definite positive correlation between magnesium and phosphorus has been established (15, 23, 44, and 159). Tucker and Smith (159) established the mean value of this positive correlation to be 0.535. This correlation was most marked in soils with a low magnesium activity as indicated by a relative low percent magnesium saturation on the exchange complex.

Bernadini and Portici (17) studied the relationship of magnesium in the translocation of phosphorus. They found that the greatest translocation was from the seed piece (after germination) to the portion of the growing plant in which it was to be used.

The role of magnesium in the movement of phosphorus within the plant has been well established (17, 158, and 166).

Webb et al. (166) found that the omission of magnesium from a nutrient solution did not retard phosphorus absorption but did have a significant effect on the movement and final location of phosphorus in plants. He also found that magnesium deficient plants were higher in phosphorus.

Willstatter (176) established the fact that during ripening of seed, magnesium increases as well as phosphorus, with a simultaneous decrease in total ash.

Longstaff and Graham (88) could find no definite correlation between available magnesium and phosphorus uptake.

If the concentration of calcium exceeds that of magnesium, increasing magnesium had little influence on the uptake of phosphorus, according to data published by Hunter (77). He concluded that the level of phosphorus in the soil was the most important factor affecting phosphorus

content of alfalfa plants. A decrease in the calcium-magnesium ratio resulted in an increase in per cent phosphorus in plants.

Truog et al. (158) stated that more consideration should be given to supplies of available magnesium so that phosphorus present in the soil might be utilized more efficiently.

The literature is in agreement, generally, that the addition of magnesium to the soil or nutrient media results in an increased per cent of phosphorus in plant material (13, 77, 114, 158, 166).

Haas (66) found that he could induce a magnesium deficiency in a nutrient solution containing 170-201 ppm phosphate unless the magnesium concentration exceeded 54 ppm.

Magnesium and Calcium Interactions.--Loew (86, 87) wrote that when soil contained more magnesium than calcium, extensive liming was necessary to prevent the soil from becoming noxious to plants. If the magnesium content is much less than the calcium content, magnesium should be added (180). It was found that cereals did best when the calcium content slightly exceeded the magnesium content. Cabbage was best when calcium was present in concentrations twice that of magnesium.

Meyer and Anderson (102) stated that excess magnesium may prove toxic in solution cultures, and this may be offset by sufficient quantities of calcium.

Cooper et al. (44) suggested that the intensity of removal of atomic ions from the soil by plants probably decreased in the following order: potassium, sodium, calcium, hydrogen, magnesium, manganese and iron.

According to Loew (87), the best ratio of calcium to magnesium by weight is seven to four.

Shive (146) studied 36 calcium-magnesium-potassium ratios and concluded that no single ratio of magnesium to calcium, magnesium to potassium or calcium to potassium determined the growth of plants. He was of the opinion that it required two of these ratios. Moser (107) could find no correlation between calcium-magnesium ratio and crop yield. Hunter (77), by decreasing the calcium-magnesium ratio, found that the per cent phosphorus in the plant increased and the available magnesium in the soil increased.

More recently, Bear (9) concluded that under uniform environmental conditions alfalfa plants had a tendency to maintain a constant milliequivalent sum of K + Ca + Mg + Na per weight of dry matter. The same was true for anions. Bailey and Drake (12) could find no effect of magnesium applied to the soil on calcium

content in blueberry leaves. Beeson et al. (15) found a negative correlation of magnesium to calcium with respect to plant uptake from nutrient solution using tomato plants.

Exchangeable magnesium was not found to be related to exchangeable calcium in the soil according to Volk (161). Zimmerman (180) concluded that the uptake of calcium is usually related to its total concentration in the soil. When magnesium is added to a soil, plants growing on the soil usually contained more calcium than where no magnesium had been applied (13, 30, 68, 80, 166).

Hashimoto (69) decreased the magnesium concentration in soybean plants by applying calcium to the soil. Nelson and Brady (110) reported similar results with ladino clover.

Magnesium and Potassium Interaction.--The exchange properties of plant roots and the metabolic effects of the plant favor a greater movement of potassium than of magnesium or calcium from the root surface into the roots and tops of plants, according to Brown and Noggle (30).

Cooper (44) found a very close correlation in a large number of plants between normal electrode potential (a measure of ionic activity) and the mineral content of plants.

The tendency is toward the plants selectively absorbing ions according to relative activity rather than relative concentrations of ions in the nutrient media (35, 43). It is further agreed that plants possess some exclusion mechanism for certain strong ions that might suppress growth.

Drosdoff and Lagasse (51) found a negative correlation between leaf magnesium and soil potassium.

A definite negative correlation between percentage composition of potassium and percentage composition of magnesium was established by Tucker and Smith (159). Potassium was shown to exert control over magnesium but not vice versa.

The importance of maintaining an optimum magnesium to potassium ratio for maximum yields has been established by several workers (33, 76, 145, 180). A wide magnesium to potassium ratio causes a potassium deficiency, whereas a narrow ratio causes a magnesium deficiency (33).

Walsh and Clarke (164) concluded that the potassium to magnesium ratio in the soil determined the magnesium uptake by tomatoes. If the ratio was high, magnesium chlorosis developed even where the culture medium was relatively high in magnesium. Johanneson (80) agreed with this finding.

According to Peech and Bradfield (119), the addition of magnesium lime to soils containing neutral salts may have no effect, may decrease, or may increase the potassium content of the soil solution depending upon the initial degree of base saturation.

Available magnesium in the soil has no effect on uptake of potassium (4, 88). However, Zimmerman (180) found that magnesium was necessary to overcome the harmful effects of too much potassium in the soil. This finding has been verified (30, 115).

Prince et al. (127) related that the most significant single factor influencing magnesium uptake by alfalfa plants was the quantity of potassium that is available for their use. As the potassium supply of a soil decreased with repeated croppings, the magnesium content of plants growing on that soil increased even when growing on a soil that was very deficient in magnesium.

The use of large quantities of potash fertilizers will increase the available potassium level of the soil to a point where magnesium uptake is so limited that plants will show definite magnesium deficiency symptoms. This fact has been established by numerous research workers (6, 26, 27, 109, 110, 149, 150, 156, 163, 165, 166, 169).

Magnesium and Nitrogen Interactions.--The role of magnesium in chlorophyll formation would indicate that there may be a definite correlation between magnesium and nitrogen. Welch et al. (169) verified this assumption and found the correlation coefficient for the magnesium-nitrogen interaction to be 0.585. This was highly significant. Boynton and Compton (28) found this positive correlation to hold even when plants were differentially fertilized with nitrogen.

Other authors (75, 113, 169) found that by increasing the nitrogen supplies available to the plant that magnesium concentration within the plant was increased.

Olson and Bledsoe (114) found a nearly constant relationship of twice as much nitrogen as magnesium oxide throughout the vegetative and reproductive organs of cotton.

Certain nitrogen containing compounds when added to the soil have a detrimental effect upon magnesium absorption. Blue and Eno (22) found that ammonia in the presence of nitrate apparently inhibits the absorption of magnesium sufficiently to produce magnesium deficiency symptoms.

McEvoy (95) using high rates of ammonia combined with a moderate or high sulfate concentration found that tobacco plants manifested a chlorosis characteristic of magnesium deficiency.

The magnesium content of leaves was decreased by soil application of ammonia or sulfate independently but to a higher degree by the former. The magnesium concentration reached the lowest level when both high magnesium and high sulfate were combined. Mulder (109) found the same relationship to exist as described by McEvoy and added that nitrates enhance magnesium absorption.

Truog et al. (158) increased the nitrogen uptake of plants by treating the soil with magnesium.

Montelaro et al. (105) found that when magnesium sulfate was applied to tomato leaves along with urea, the urea intake decreased from twenty-nine per cent to six per cent as compared to urea alone. The magnesium sulfate was also instrumental in reducing the injury caused by urea.

Other Magnesium Interactions.--The addition of sulfur to the soil in any form increases the prevalence of magnesium deficiency. Where the deficiency is already in evidence sulfur additions in the form of sulfates make the deficiences worse (62, 95, 109, 164).

Carolus (35) reported that plants selectively absorb sodium in preference to magnesium. Other investigators found that sodium addition reduced the magnesium uptake by plants (44, 82).

Sanik et al. (137) found that a high level of magnesium in the soil favors the uptake of boron,

manganese and zinc. Jones (81) concluded that magnesium lime suppressed boron availability more than calcium lime. Shear et al. (144) offered an explanation of this disagreement. A high ratio of calcium and potassium to magnesium consistently resulted in boron toxicity and that a high ratio of calcium and magnesium to potassium was even worse. A high potassium and magnesium to calcium ratio has little effect on appearance of boron toxicity.

Effect of Magnesium on Symbiotic N-fixation

Graham (65) found that magnesium increased the fixation of nitrogen symbiotically in soybean plants by stimulating bacterial activity to a much greater degree than did equal quantities of calcium compounds.

Fixation of nitrogen by legumes growing on nutrient media to which magnesium had been added was insignificant unless extra calcium was available, according to Albrecht (2). He believed that the symbiotic organisms were acclimated to plants accustomed to a high level of soil fertility in the form of calcium, magnesium and other mineral nutrients. The indirect effect of magnesium on nitrogen fixation by legumes was in the release of calcium.

Available magnesium was found to increase the nitrogen fixing power of legumes (83, 88).

Methods

The standard method for determination of magnesium in soil and plant material listed in A.O.A.C., in which magnesium is precipitated as $Mg_2P_2O_7$, is very long and tedious. The method is accurate if the procedure is followed to the letter and co-precipitation of other cations, especially manganese, is accounted for (3).

The time required for a single determination practically prohibits its use in routine soil and plant analysis and provides a very good reason for further investigations into an accurate but faster method.

Various volumetric and colorimetric procedures have appeared in the literature with various methods of circumventing or removing interfering ions. These methods are good but the time required to remove certain ions or compensate for them is very great and little time is saved over the standard A.O.A.C. method. Many of the methods proposed for removing interferences are not complete in that one or more ions causing interference were not accounted for.

Willson (173) proposed a fairly simple volumetric titration of magnesium using the perchloric-nitric acid digest of plant material. Results compared favorably with the oxine method for determination of magnesium.

In 1940, Peech (118) introduced a modification of Kolthoff's colorimetric method using titan yellow to develop a pink lake. The color of the pink precipitate being proportional to the concentration of magnesium in the solution. Peech did not recommend the method for precise quantitative work because calcium was a major source of error and the ammonia ion would completely prevent the formation of the lake. Manganese, iron, aluminum, zinc and copper were also found to interfere. Sodium or ammonium acetate extracts for available cations would not contain sufficient quantities of these ions to cause serious interference; however, in a total soil analysis these ions would be present at sufficient concentrations to cause serious errors. Weeks and Todd (167) reported that iron, aluminum and calcium interfere and could be separated using ammonium hydroxide and ammonium acetate.

In 1950, Abrahamczik (1) also reported that iron, aluminum, calcium, phosphorus and manganese were found to interfere with the titan yellow method. He did not mention zinc and copper ion interference previously reported by Peech.

Willson and Wander (174) found that the addition of potassium cyanide to both the standards and unknowns would eliminate copper interference.

Yien and Chesnin (178) proposed a modification of the titan yellow method that increased the stability of the colored lake from one hour to 24 hours. The order of adding reagents was very critical and concentration of ammonium acetate had to be controlled very closely to avoid error.

Drosdoff and Nearpass (52) using thiazol yellow and a starch compensating solution, found that iron, aluminum, manganese, phosphorus and calcium interfered very much the same as reported for titan yellow.

Mikkelsen et al. (104) added the ammonia ion to the above list of interfering ions and then found that results obtained by using this method were about three per cent higher than the A.O.A.C. method for soils while recoveries from plant material ranged from 94 to 105 per cent.

In 1950, Sterges and MacIntire (152) compared 130 organic compounds for possible use as dyes for the magnesium determination and concluded that thiazol yellow was best by far. They reported that calcium up to 2.46 per cent in plants had no effect. Manganese and iron had no effect and concentration in plants was below 0.15 per cent. Aluminum interfered when concentration exceeded 0.08 per cent in air dry material. Perchloric acid caused a fading of the color.

In the past few years the flame spectrophotometer offered a means of quantitative analysis and has been refined through the use of quartz prisms, improved burners, hotter flames, and an elaborate photomultiplier to step up the sensitivity several fold. This instrument and the flame photometer have been used for the determination of sodium, potassium, calcium and lithium for several years.

Rogers (135), using a quartz photoelectric spectrophotometer in conjunction with an air acetylene flame from a Lundegardt burner, reported that flame values for calcium and potassium did not vary from the chemical values using a normal ammonium acetate extract.

In 1948, Parks et al. (116) tested the effect of twenty-one different cations upon the determination of sodium and potassium as well as six acids. All were found to interfere at one concentration or another.

Bills (18) reported that excess sodium produced high or low potassium results depending upon the concentration of potassium being tested. All other reports are that sodium enhances the potassium flame regardless of potassium concentration being tested (18, 56, 141, 170).

Most articles agree on a general enhancement or depression of one ion upon another. The effect of extraneous cations upon the sodium, potassium and calcium determination have been discussed at great length in the

following references: (8, 18, 31, 32, 39, 53, 64, 93, 108, 112, 125, 132, 141, 143, 170).

The effects of various anions upon the flame intensity of sodium, calcium and potassium have been investigated but not to the extent of the cation investigations.

Margoshes and Vallee (93) reported that the potassium flame was not affected by the following ions: nitrate, chloride, oxalate, phosphate or sulfate. West and False (171) agreed with this finding. It was further observed (64, 170) that the effect of anions upon the sodium flame are very much the same as for potassium.

Calcium, unlike sodium and potassium, creates quite a problem in flame analysis due to the many anions that cause interferences. The literature is very much in agreement in respect to anion interference upon this element. Phosphate and sulfate ions always produce a depressing effect on calcium emission, regardless of the concentration of the anion or calcium (5, 39, 54, 64, 84, 93, 112, 125, 132, 170).

The perchlorate ion is the only anion that produces an enhancement to the calcium flame emission. All of the other anions studied have a depressing effect. The magnitude of the depression varied with the anion. The following anions that produce a depressing effect are listed in descending order according to the magnitude of the effect;

phosphate, sulfate, arsenate, nitrate, chloride, borate and oxalate (5).

Sulfate, phosphate and arsenate depress the calcium flame emission up to a certain concentration; however, with concentrations in excess of this no further depression is noted. Whereas, the perchlorate ion produces an enhancement up to a certain concentration and if added in excess of this does not further enhance the calcium flame. This indicates that there is chemical bonding that is very definite for each of these ions with calcium which the energy of the flame is unable to break.

The effect of both anions and cations upon the magnesium flame emission have not been reported in the literature except very briefly.

Brown et al. (31), using the 371 millimicron line for magnesium, noted that neither potassium, sodium nor chloride had any effect upon the magnesium emission at this line. The same authors later reported that the 285.2 millimicron line could be used for the determination of magnesium with very little interference from elements normally found in plant ash solutions. They determined that calcium up to 800 ppm, potassium up to 600 ppm, and sodium up to 200 ppm had no effect on magnesium emission at this wavelength. Flame analysis varied about three per cent from chemical analyses (volumetric method).

Rich (132) reported that iron, calcium and sodium caused significant interferences at the 371.0 millimicron line when magnesium concentration was below 2.0 meq. per 100 grams (240 ppm). At the 2852 millimicron line, calcium in excess of 8 meq. per 100 grams depressed the magnesium flame intensity. Iron and aluminum in concentrations exceeding 100 ppm, slightly suppressed magnesium emission. Potassium, manganese, iron, sulfur and silicon produced no effect at the 285.2 line in concentration normally found in normal ammonium acetate extract.

Thirty-two soils were analyzed using the flame and the analyses were compared with standard chemical methods by Shaw and Veal (143). The flame results were very comparable except that the flame values were about 0.1 meq. lower than the values determined chemically by precipitation.

Noebels (112) found, by dissolving a sample of cast iron in concentrated nitric acid and removing both iron and phosphate as iron phosphate, the magnesium results were very reliable. He used electrolysis to separate all elements below aluminum in the electromotive series.

Iron was separated from magnesium and other bivalent metals as basic formate using urea in a technique developed by Willard (174).

Dean and Lady (47), using acetylacetone to selectively extract iron, found that the acetone acted as a chelating agent as well as a solvent. The sensitivity was increased because of the lower viscosity and lower boiling point of the acetone that was being passed through the flame.

Several authors (5, 54, 84, 125, 141, 170) have advocated the use of radiation buffers as a method of getting around interferences. In this method large amounts of the ions not being determined are added to standards and unknowns alike. The additions of large amounts of these ions are supposed to provide uniform radiation characteristics to the flame.

Radiation buffers are very good for the sodium and potassium determination, since the energy required to excite these ions is very low and instrument sensitivity is not a problem. The energy required to excite calcium and magnesium ions is very large and the use of radiation buffers is a big draw on the available energy in the flame. The result of adding these buffers to the solution that is passed through the flame is a lowered instrument sensitivity, especially with anion buffers.

The Beckman DU spectrophotometer with a photomultiplier attachment is sensitive enough for calcium so that the loss of sensitivity is not too great a factor.

This is not true for magnesium and especially if the 285.2 millimicron wavelength is used. The Beckman model B does not have the sensitivity for calcium that is required for practical use of these buffers, especially when the calcium concentration being determined is low.

Baker and Johnson (5) proposed the addition of an excess of the predominant ions present to eliminate anion interference. He did not mention the tremendous loss of instrument sensitivity or the effect due to other ions present in lower concentrations.

Krienke and Gammon (84) removed sulfate and phosphates by lead precipitation. They also used radiation buffers to compensate for the cation interferences.

The ideal method of getting around ion interference is by removing the ion that is causing the trouble. In many cases, where the ions cannot be separated, it is possible to eliminate the effect by further dilution of the sample or using a higher concentration of standards for comparison of the unknowns.

Anions can be quantitatively separated from cations by the use of exchange resins. Since the anion effect is so much greater than the cation effect, most of the trouble can be eliminated by the use of anion resins.

Geheke et al. (64) used Amberlite IR-4B-Cl, a high phosphate capacity resin, to remove anions and reported

good results for the potash determination.

Dow Chemical Company has published two bulletins (48, 49) concerning anion exchange resins and the mechanism of their resins exchange properties.

EXPERIMENTAL PROCEDURE

Methods

Instrument Description.--A Beckman DU quartz spectrophotometer with a model 4304 photomultiplier, a model 1900 battery charger-voltage stablizer attachment, and a model 9220 flame attachment were used for all of the magnesium determinations. The burner-atomizer assembly was a model 4030, used in conjunction with oxygen utilizing hydrogen as fuel.

Research on the flame determination of magnesium has been minimized due to the lack of sensitivity of the older instruments and also to the fact that magnesium is more difficult to excite than sodium, potassium, or calcium.

The development of the photomultiplier tube has increased the sensitivity of the instrument so that magnesium determinations are now possible. Most of the previous work was done using the oxygen-acetylene, air-acetylene, oxygen-propane, or other gas and oxygen combinations.

The knowledge of the effect of other ions upon the determination of sodium, potassium, and calcium has stimulated investigations regarding the effect of ions encountered in

soil or plant extracts on the determination of magnesium, using the latest and most sensitive instrument with the hotter oxygen-hydrogen flame.

The various types of interferences which have been encountered have been discussed in the review of literature.

There are three possible wavelengths that can be used in the determination of magnesium with the Beckman DU flame spectrophotometer. The 371 and the 383 millimicron lines are the wavelengths at which the emission of a molecular band, usually emitted by an oxide of the metal, is at a maximum. These are known as band lines and are usually complex, fairly broad, and asymetric. One of these lines must be used unless the instrument is equipped with a photomultiplier. By using a multiplier tube the sensitivity of the instrument is increased so that the 285.2 millimicron line, which is in the ultraviolet region of the spectra, becomes the third possible wavelength for magnesium. This line is an arc line or a line that is produced by the emission from a neutral atom.

The purpose of part of this study was to determine which of the three lines is most free from the effects of extraneous ions. Should a specific ion interference appear at one of the wavelengths and be absent at one of the others, this knowledge would be of value in circumventing the interference.

Instrument Calibration.--Before the actual interference study was undertaken the oxygen pressure was held at the pressure recommended by the manufacturer; the hydrogen pressure was set at intervals of one, two, three, six and ten psi to determine which fuel setting gave the best curve. Standards containing 0, 10, 20, 30, 40, 50, 100 and 250 ppm magnesium were used to test these various pressures. The standards were prepared by dilution from a 1,000 ppm magnesium standard made by dissolving 1.6579 grams of magnesium oxide (C.P.) in enough concentrated hydrochloric acid and diluting with distilled water to give a final volume of 1,000 ml. of 0.1 N HCl solution. The different curves obtained from this study are given in Figure 1.

It is evident from Figure 1 that both the four and six pound hydrogen pressures resulted in curves with greater slopes. The slit width of the two, three, four and six pound hydrogen pressures were 0.140 mm., 0.090 mm., 0.050 mm., and 0.035 mm., respectively. The sensitivity control was about six turns from the counter-clockwise limit for these slit settings.

By opening the hydrogen neddle valve slightly and making more of the fuel available to the flame it was found that a three pound hydrogen pressure would give a curve with the same slope as was obtained with the six pound pressure shown in Figure 1. A curve obtained using this technique

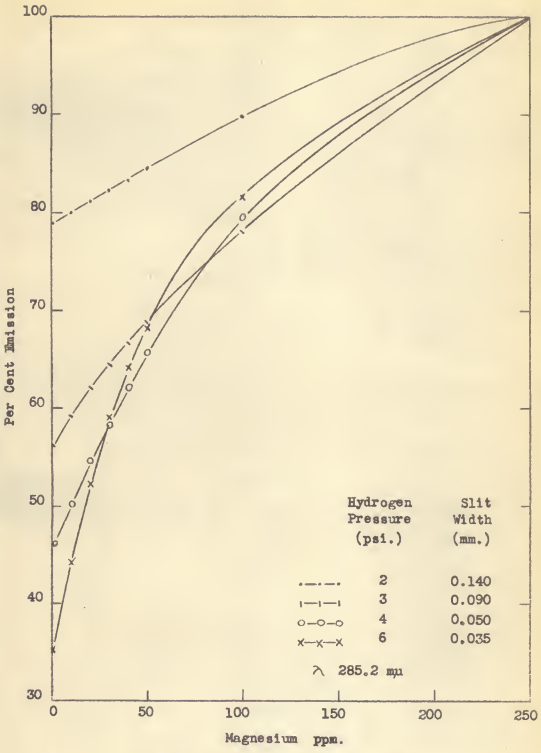

Fig. 1. The Effect of Various Hydrogen Pressures on the Standard Curve for the Magnesium Determination.

is shown in Figure 2. The lower pressure results in a greater saving of hydrogen with no appreciable difference in the standard curve.

The sensitivity of the instrument was determined at various positions of the sensitivity knob. The stability of the instrument was greatest when the sensitivity knob was turned to the counter-clockwise limit; however, the values obtained are not nearly as reproducible as values obtained when the control was at its clockwise limit. This is emphasized in Table 1.

TABLE 1

THE EFFECT OF VARIOUS SETTINGS OF THE SENSITIVITY CONTROL ON THE STABILITY AND SENSITIVITY OF THE SPECTROPHOTOMETER

Needle Stability	Number of Turns Clockwise	Galvanometer Sensitivity in Per Cent Transmission/ Scale Division
Erratic	10.0	1/2.0
Erratic	8.5	1/1.5
Slightly erratic	6.0	1/1.0
Stable	2.0	2/1.0
Stable	0.3	3/1.0
Very stable	0.0	5/1.0

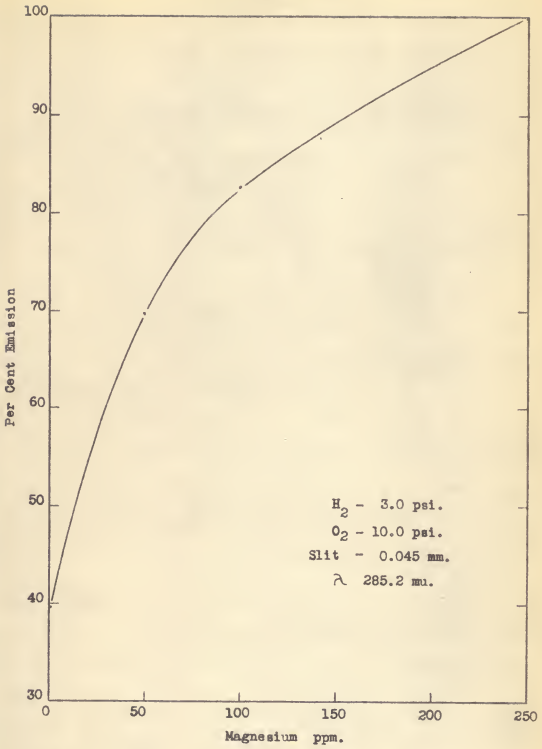

Fig. 2. Calibration Curve for the Magnesium Determination at the Hydrogen and Oxygen Pressures Used Throughout Most of this Work.

From the data presented in Table 1 it was decided to set the sensitivity control from six to nine and one-half turns clockwise. Even with the unstable galvanometer needle, the values were very reproducible. This was not the case when the sensitivity control was at its counter-clockwise limit. At this limit the values varied about five per cent in transmission between several readings on the same solution. At the clockwise limit, the values did not vary one-half of one per cent transmission between several determinations on the same solution.

Considering all of the above findings, it was decided that all of the interference studies with this instrument would be run at the following settings; slit width, 0.030 mm. to 0.050 mm.; sensitivity control, six to nine and one-half turns clockwise; photomultiplier at full sensitivity; hydrogen pressure at three pounds per square inch; and oxygen pressure at ten pounds per square inch.

Standard Solutions.--All of the salts and acids that were used in making up the standard solutions, with and without the interfering ions, were made from reagent grade chemicals of the highest purity available. Table 2 lists the chemicals used and other information regarding the amount weighed out and how the salts were dissolved.

TABLE 2

CHEMICAL FORMULAS, WEIGHTS USED, CONCENTRATIONS OF STOCK SOLUTIONS AND THE METHOD OF DISSOLVING THE ELEMENTS OR COMPOUNDS USED IN MAKING STOCK SOLUTIONS

Formula of Salt or Acid Used	Grams or Milliliters of Salt or Acid Per Liter of Solution	Concentration in ppm of the Ions in Stock Solution	Milliliters of Concentrated HCl and Method of Dissolving
MgO	1.6579 gms.	1000 ppm Mg	8.5 + Heat
Fe (metal)	1.0000 gms.	1000 ppm Fe	8.5 + Heat
KCl	1.9060 gms.	1000 ppm K	8.5 -
$NaCl$	5.0836 gms.	2000 ppm Na	8.5 -
$KMnO_4$	2.8769 gms.	1000 ppm Mn	8.5 -
H_2SO_4	3.46 ml.	2000 ppm S	8.5 -
K_3PO_4	4.35 ml.	2000 ppm P	8.5 -
$CaCO_3$	2.4973 gms.	1000 ppm Ca	8.5 + Heat
$CuCl_2$	4.2322 gms.	2000 ppm Cu	.....
HCl	Conc. reagent	Various Dilutions	8.5 -
Al (metal)	1.0000 gms.	1000 ppm Al	8.5 + Heat
K_2SiO_3	2.7826 gms.	1000 ppm Si	Dissolved in KOH and Acidified
HNO_3	1.03 ml.	1000 ppm NO_3	8.5 -
ZnO	1.2446 gms.	1000 ppm Zn	8.5 -
$HC_2H_3O_2$	17.6 Molar	Various Dilutions	8.5 -
$HClO_4$	11.99 Molar	Various Dilutions	.....

The method used to measure the effect of various ions on the magnesium flame emission was to study the ions individually and then in combinations. Five series of standards containing 0, 50, 100, 250 and 500 ppm magnesium were prepared by dilutions from the stock solutions described in Table 2. The first series contained only the magnesium ion with no interfering ion present and was the curve used to test the effect of the ion under investigation. Since the first series contained none of the ion being tested for interference (iron for example), it was called the 0 ppm interference-ion series. The next four series contained 50, 100, 250 and 500 ppm of the interference-ion. The explanation is more easily understood by examination of Table 3 which gives the method of preparing standards for the measurement of the effect of iron on the magnesium flame emission.

All of the standards used in this study were prepared in the same general manner except the dilutions and concentrations varied somewhat from the example in several cases. It may be seen from this table that magnesium increases horizontally across the table and iron increases down the columns. By setting up the experiment in this manner, it was possible to obtain the effect of iron on the magnesium flame when the iron concentration is less than, equal to, or greater than the magnesium concentration, and vice versa.

TABLE 3

DILUTION TABLE USED IN PREPARATION OF STANDARDS USED TO DETERMINE THE EFFECT OF IRON ON THE MAGNESIUM FLAME EMISSION

Iron ppm	Each Entry is the Number of Milliliters of 1000 ppm Stock Solutions Required per 100 Milliliters to Give Desired Concentration				
	Magnesium ppm				
	0	50	100	250	500
		(5 ml.)	(10 ml.)	(25 ml.)	(50 ml.)
0	0 ml.	0 ml.	0 ml.	0 ml.	0 ml.
50	5 ml.	5 ml.	5 ml.	5 ml.	5 ml.
100	10 ml.	10 ml.	10 ml.	10 ml.	10 ml.
250	25 ml.	25 ml.	25 ml.	25 ml.	25 ml.
500	50 ml.	50 ml.	50 ml.	50 ml.	50 ml.

Procedure for Interference Studies.--The results of the experiment on the effect of iron on the magnesium flame are reported in Table 4. This table will also serve to demonstrate the procedure followed in studying the effect of iron as well as the other elements investigated.

TABLE 4

THE EFFECT OF VARIOUS CONCENTRATIONS OF IRON ON THE PERCENTAGE EMISSION OF THE MAGNESIUM FLAME

Iron ppm	Per Cent Emission				
	Magnesium ppm				
	0	50	100	250	500
0	32.0	56.8	66.3	84.8	100.0
50	32.0	56.8	66.3	84.8	100.0
100	32.0	56.8	66.3	84.8	100.0
250	32.0	54.8	66.0	82.6	98.8
500	32.0	54.6	66.0	82.2	98.0

In obtaining the data in Table 4 the instrument was adjusted to read 100 percent emission on the 500 ppm magnesium standard that contained no iron. This is the setting on which all of the other values in the table are based. It was checked after each reading. Using this setting for the instrument calibration, and since all of the

solutions in that column contained the same concentration of magnesium with increasing amounts of iron all of the values in this column should read 100 per cent emission if there is no effect due to iron.

Using the 500 ppm magnesium standard containing no iron the instrument was set to read 100 per cent emission. Using this setting, the 250 ppm magnesium solution was inserted under the burner and its reading taken. It was found to read 84.8 per cent emission. By the same reasoning, if the iron exerted no effect on the magnesium flame then all of the values reported in this column should read 84.8 per cent emission. The same was repeated for all of the magnesium concentrations. The column containing no magnesium with increasing concentrations of iron read 32.0 per cent emission regardless of the iron concentrations. At the 285.2 millimicron line this is typical in that other ions do not add to or subtract from the background. The hydrogen flame itself produces only a very slight background.

There was no effect on the magnesium flame due to iron until the iron concentration was 250 ppm or above and then it produced a depressing effect. All of these data were obtained using the 500 ppm magnesium solution as the top standard. The next step was an attempt to determine what effect the same concentrations of iron would have using the 250 ppm magnesium as the top standard. In this study all

of the 500 ppm magnesium solutions were discarded and the same procedure, already described, was repeated. All of the 250 ppm magnesium solutions were discarded and the 100 ppm magnesium solution containing no iron was set to read 100 per cent emission. The results of this experiment are reported in Table 5.

TABLE 5

EFFECT OF IRON ON MAGNESIUM FLAME EMISSION USING 100 PPM MAGNESIUM AS THE TOP STANDARD

Iron ppm	Per Cent Emission		
	Magnesium ppm		
	0	50	100
0	46.4	84.5	100.0
50	46.4	84.5	100.0
100	46.4	84.5	100.0
250	46.4	78.0	94.4
500	46.4	77.6	93.4

Table 5 indicates that by reducing the magnesium concentration in proportion to the iron concentration, the depression due to the iron has been increased. When the 50 ppm magnesium was set to read 100 per cent emission, the same 50 ppm magnesium solution containing 500 ppm iron read

87.2 per cent emission instead of 93.4 as was the case with the 100 ppm magnesium solution containing 500 ppm iron.

This same procedure was repeated exactly as described above using each of the three possible wavelengths.

The effect of increasing the slit width was studied by using the procedure described above. Each time the magnesium concentration was reduced, the slit had to be opened in proportion. The slit could also be held constant at the different magnesium concentrations by increasing the sensitivity using the sensitivity control. Both techniques were used at each of the three wavelengths.

The 100 ppm magnesium solution containing 250 ppm iron read 94.4 per cent emission based on the 100 ppm magnesium solution containing no iron. The 100 ppm magnesium solution containing 250 ppm iron was then set to read 100 per cent emission to determine whether or not it would read the same as the 100 ppm magnesium containing no iron. The readings were found to be identical. This indicates that the depressing effect is due to part of the energy available in the flame being required to excite the iron at the expense of magnesium excitation. Iron oxides have a high melting point (1535° C) and a very high boiling point (3000° C). In the flame, the iron enters the burner in the form of iron chloride. On entering the flame the water evaporates and the chloride is lost immediately

leaving a mixture of salts and elemental iron or oxides of iron. In the flame, decomposition or other chemical reactions occur. Then the salts or their decomposition products dissociate. Not until after all of these events have taken place can the metal be excited to form molecules (oxides of metals) which are then excited. All of these steps must take place practically instantaneously. All of the ions in the original solution compete for the energy available in the flame. This explains the depressing effect produced by higher concentrations of iron. As the concentration of iron increases the energy required to excite it increases and less energy is available to excite the magnesium atom.

Five curves, one for each concentration of ion studied, were drawn from the data obtained at three wavelengths and at two concentrations of magnesium. Five concentrations of magnesium were used; however, only the 500 ppm and the 100 ppm magnesium curves are reported. The 100 ppm magnesium curves were selected because all of the unknowns were determined using a 100 ppm standard. The 500 ppm standards were used to determine the effect of the added ion at high concentrations of magnesium.

Anion Separation Employing Resins.--Dowex 1, an anion exchange resin, was used in the following study. Known solutions containing magnesium with sulfur and phosphorus as

interfering ions were passed through a 5-inch column of resin. The tubes were made from soft glass with an inside diameter of nine mm. and a total length of 230 mm. The bottom of the tubes were tapered to approximately 1.5 mm. inside diameter at the bottom to hold the glass wool and to slow down the rate at which the solution passed through the resin.

The tapered end of the tube was inserted into a small piece of rubber tubing connected to an aspirator. With the aspirator running, a small piece of glass wool was compressed and sucked into the tube until it reached the restricted area where it was held. The tube was then inserted into a beaker containing resin. The resin was drawn up into the tube until it reached the 5-inch mark and the tubes containing the resin were then tamped two or three times to fill any large air spaces that might have been present.

The columns were then placed in filter racks and 5 ml. flame beakers were used to collect the leachate from each tube. Individual tubes were used for each sample solution. The leachate in each beaker was stirred after passing through the resin.

An experiment to determine how much phosphorus the resin would remove from four plant ash solutions at two different dilutions was set up. Two sample solutions

containing the highest percentage phosphorus and two containing the lowest were selected. These solutions were passed through the resin columns and the first, second, third, fourth, fifth and sixth four-millimeter fractions were taken individually and analyzed for calcium, magnesium and potassium using the flame method. Phosphorus was determined using the ammonium molybdate-stannous chloride method (157).

Source of Soil and Plant Material

Greenhouse Experiment.--An experiment to determine the effect of six levels of magnesium on the growth of oats was set up in the greenhouse where the growing conditions could be more closely controlled. Care was taken to eliminate any variation which might be due to moisture and loss of magnesium or other ions by leaching.

Jonesville fine sand, known to be deficient in magnesium from a previous minor element experiment conducted by the Soils Department, was used in this experiment. The soil was very carefully mixed to insure a homogenous mixture of all the minor elements that had been added prior to this experiment. Seventeen pounds of soil were added to 18 two-gallon pots. Demineralized water was added until the soil, as observed through the hole in the bottom of the pot, was moist and thereafter when the top of the soil appeared dry.

On February 8, 1955, twenty-four Seminole oat seeds were planted per pot. After germination the stand was thinned to twelve plants per pot. Fertilizer was applied at the time of planting in solution form. Each pot received nitrogen equivalent to 100 pounds per acre, phosphorus equivalent to 25 pounds per acre, and potash equivalent to 50 pounds per acre. These rates were applied after each cutting. Magnesium was added at rates equivalent to 0, 15, 30, 60 and 120 pounds per acre magnesium as a solution of magnesium sulfate. The magnesium was applied only at the start of the experiment.

Each of the six rates of magnesium was replicated three times. The treatments were randomized within each replication. Observations were made periodically to determine the effect of the treatments on the oat growth. The first cutting was taken March 18, 1955. All plants were clipped to about one inch above the soil level and the soil was fertilized immediately as described above. The last cutting was taken after the seeds were mature so that a seed yield could be taken.

The cuttings were allowed to dry in paper bags in the greenhouse. After two weeks, the plant samples were dried in an oven and weighed for yield. The content of each bag was ground in a Wiley mill to pass a two millimeter seive and stored in glass jars until it was analyzed.

After the last oat harvest, the soil in each pot was allowed to dry and then mixed thoroughly on a large piece of heavy wrapping paper. A one pint sample of soil was removed by taking several small samples at random from the pile of soil.

The soil was then poured back into the pots, re-fertilized as described above, except for the magnesium, and planted to soybeans. Six seeds were planted per pot and thinned to two plants soon after germination. Yields were taken at the bloom stage. Soil samples were taken, as described above, for chemical analyses after the soil had dried.

Field Experiment.--A randomized block design was used to determine the effect of six levels of magnesium from two sources applied to Klej fine sand on yield and nutrient uptake by soybeans in the field. Six levels of magnesium from each of the two sources were replicated four times and the levels were randomized within each replication. The entire experimental area of approximately one-seventh of an acre was divided into 48 plots, each nine by fifteen feet in size. The experiment was carried out at the Suwannee Valley Experiment Station in Suwannee County.

The experimental area received a uniform application of high calcic limestone at a rate equivalent to one ton per acre. A uniform application of 0-10-20 fertilizer was

broadcast over the area at a rate equivalent to 600 pounds per acre. The fertilizer and lime were applied one day prior to planting and the area disced twice, the second discing being in a direction at right angles to the first. Following the discing, magnesium was added to each of the individual plots at rates equivalent to 0, 30, 60, 120, 240 and 480 pounds per acre.

Soybeans of the Jackson variety were planted June 30, 1955 in rows three feet apart and running the long dimension in the plot. The outside row and a single row between each plot served as border rows and the remaining two rows in each plot were harvested. One row was harvested at the bloom stage to determine the yield of plant material and the remaining row was left until maturity to determine the seed yield.

Plants were harvested September 14, 1955 when the first seed pods appeared. The entire plant was clipped to about one inch above the soil using hand clippers. Two stakes tied exactly ten feet apart were used to measure the portion of the row to be harvested for the yield determination. The clippings from the ten foot row were weighed on a standard milk scale. Twelve plants were selected at random to be analyzed chemically. Five of the 48 samples collected in this manner were weighed immediately after harvest for moisture determinations. The five samples were

then placed in a drying oven for 24 hours and reweighed. The per cent moisture was calculated from these weights. The average per cent moisture determined for the five was used in the dry matter calculations for all 48 samples.

The samples that were not used in the moisture calculations were allowed to dry in the greenhouse for two weeks and then placed in the drying oven over night. The following morning the samples were ground in a Wiley mill to pass a two millimeter seive and stored in labeled two ounce bottles.

The remaining row in each plot was harvested after the seed had matured. Seeds were separated from the plants and hulls using a small thresher. The beans were cleaned and weighed. The weights were then converted to bushels per acre using the standard weight per bushel for soybeans.

Ten soil samples from each plot were taken and mixed into a single composite sample. The soil plugs were taken to a depth of six inches using a soil sampling tube. The composite samples were carried to the laboratory where they were placed on large squares of wrapping paper and allowed to air dry for two weeks. The samples were then screened through a 20 mesh screen and mixed thoroughly before being stored in pint ice cream containers. The samples were again mixed prior to the removal of a sample for analysis.

RESULTS AND DISCUSSION

Interfering Ions

The effect of the added ions on the magnesium flame emission will be discussed in the order that they were determined in the laboratory. The ions will be discussed individually in the first part and then the effect of the addition of two ions simultaneously known to cause interference will be discussed.

Effect of Potassium on the Magnesium Flame.--The potassium ion exerted an enhancing effect upon the magnesium flame emission at the 371.0 millimicron wavelength. This enhancing effect was due to the background produced by the potassium flame and the enhancement increased as the potassium concentrations increased. The presence of as little as 50 ppm potassium produced a very serious error in the magnesium determination at this wavelength when the highest magnesium standard was 100 ppm as shown in Figure 3. Using this magnesium standard the presence of 50 ppm potassium produced an error of about six per cent and the presence of 500 ppm potassium produced a reading that was about 16 per cent higher than the true value. When the highest magnesium standard was 50 ppm, the presence of

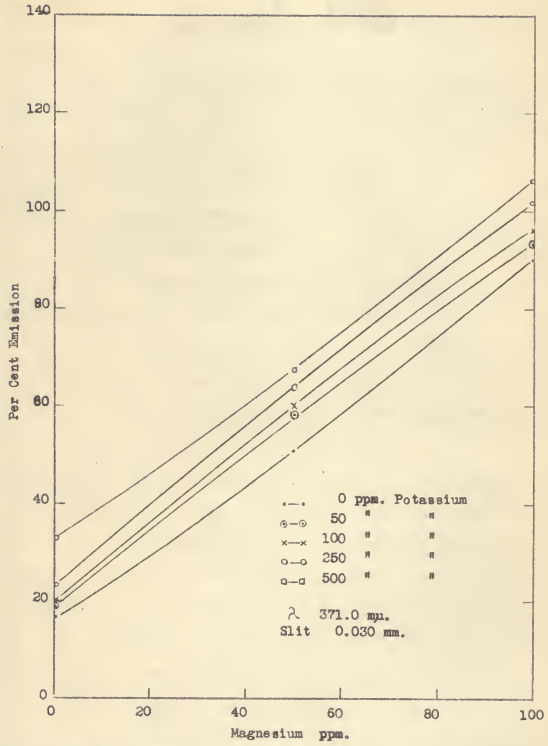

Fig. 3. The Effect of the Potassium Ion on the Magnesium Flame Emission at the 371.0 mμ. Wavelength.

500 ppm potassium produced a 24 per cent higher reading than the true value.

When the highest magnesium standard was 500 ppm, the background produced by 500 ppm potassium was five per cent as shown in Figure 4. The increase was the same in the standards containing no magnesium as was found in the highest magnesium standards.

The effect of potassium on the magnesium flame emission at the 383.0 millimicron wavelength is shown in Figure 5. Henceforth, the 100 ppm magnesium curves will be discussed first because the highest concentration of the standards used in comparing the unknowns was 100 ppm magnesium. The 500 ppm magnesium curves will be mentioned briefly. The background enhancement produced by 500 ppm potassium on the 100 ppm magnesium curve is the same type of enhancement as found at the 371 millimicron wavelength but of greater magnitude. Here the enhancement is 20 per cent and is the same at the low concentration as at the high concentration. The same concentration of potassium produced an enhancement of about 29 per cent on the 60 ppm magnesium curve. This effect is not so great when the magnesium concentration is equal to or greater than the potassium concentration. This fact is shown in Figure 6. The enhancement here is eight per cent even at the 500 ppm potassium concentration.

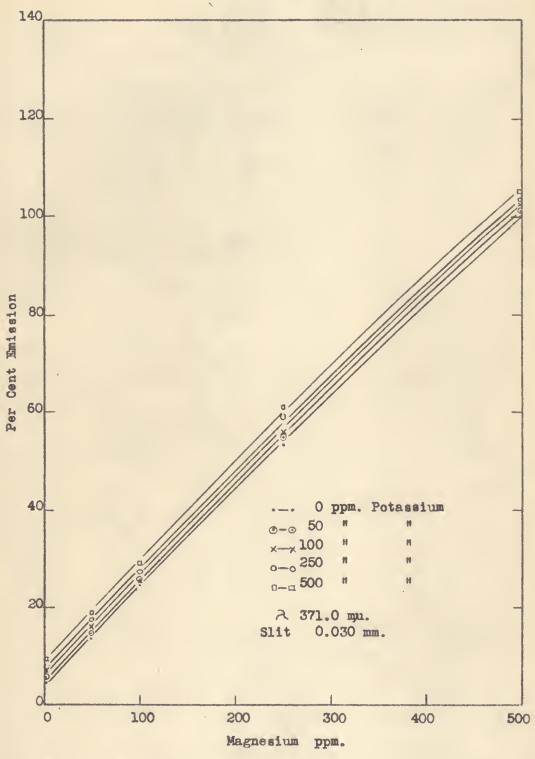

Fig. 4. The Effect of the Potassium Ion on the Magnesium Flame Emission at the 371.0 mu. Wavelength.

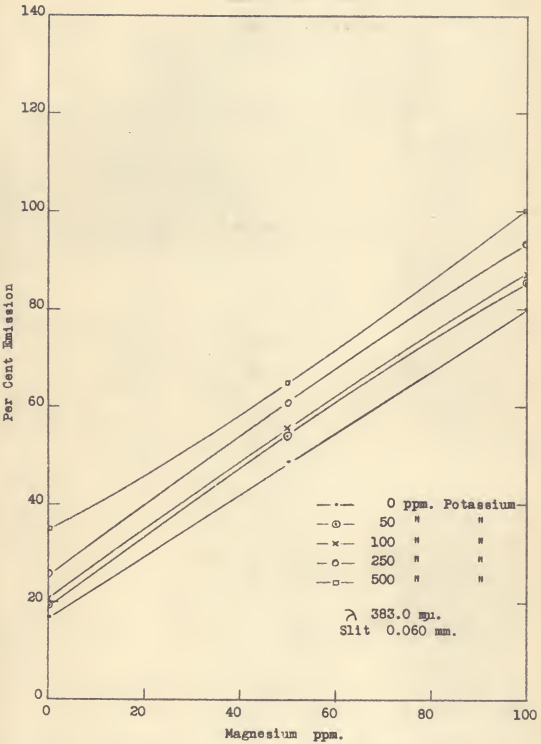

Fig. 5. The Effect of the Potassium Ion on the Magnesium Flame Emission at the 383.0 mμ. Wavelength.

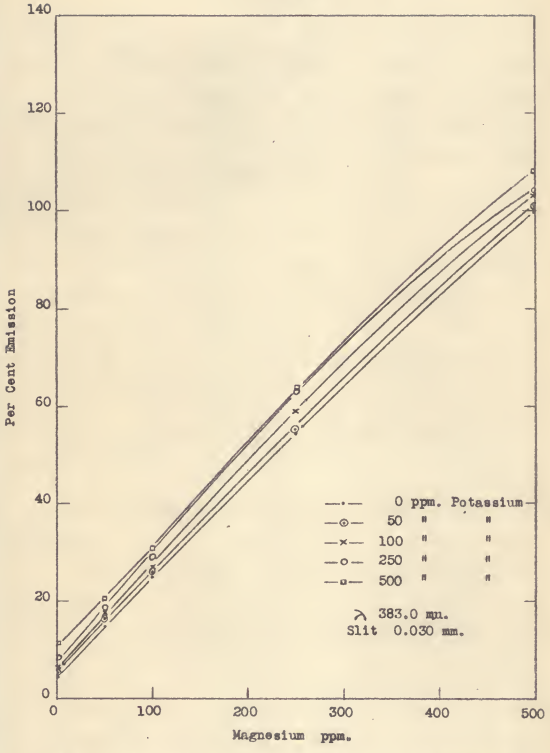

Fig. 6. The Effect of the Potassium Ion on the Magnesium Flame Emission at the 383.0 mμ. Wavelength.

It is obvious from the examination of these curves that unless the background enhancement due to potassium could be compensated for, the 371.0 and 383.0 millimicron wavelengths could not be used.

The only remaining wavelength, the 285.2 millimicron line, and the weakest of the three from the radiation standpoint was then tried. The results obtained were very interesting as shown in Figures 7 and 8. There was no effect produced by potassium on the magnesium flame at the concentrations studied at any of the magnesium concentrations used. This wavelength was far superior to either the 371.0 or the 383.0 millimicron wavelength when the solutions being determined using the flame contained potassium.

The Effect of Iron on the Magnesium Flame.--The effect of iron on the magnesium flame emission at the 371.0 millimicron wavelength is a combination of background and radiation effect as shown in Figures 9 and 10. The presence of 50 ppm iron in the 100 ppm magnesium standards produced a four per cent enhancement on the zero ppm magnesium solution and an eight per cent depression on the highest magnesium solution. In the solution where only the 50 ppm iron was present, there was enough dissociation of the iron

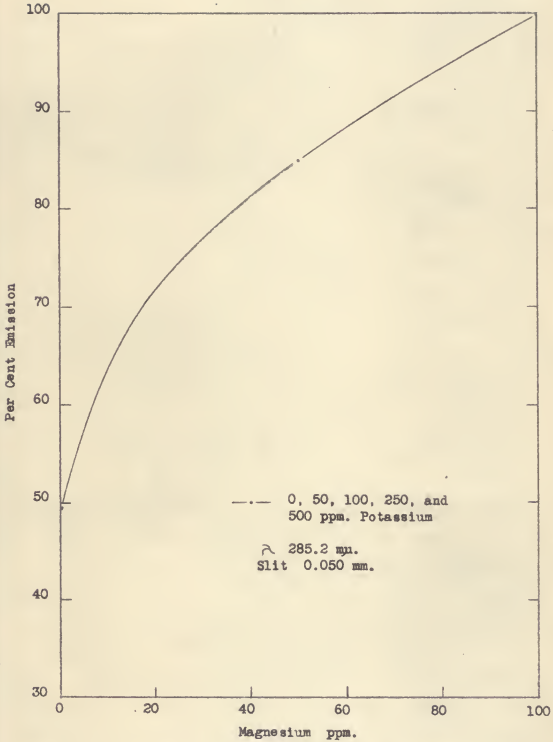

Fig. 7. The Effect of the Potassium Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

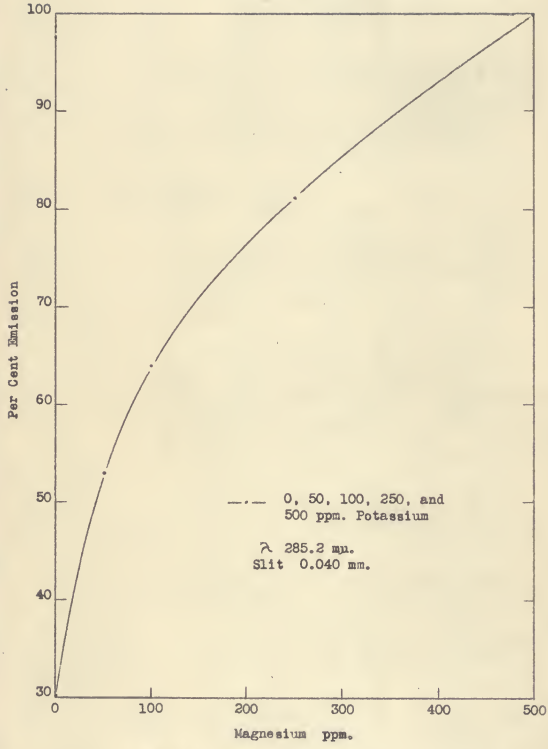

Fig. 8. The Effect of the Potassium Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

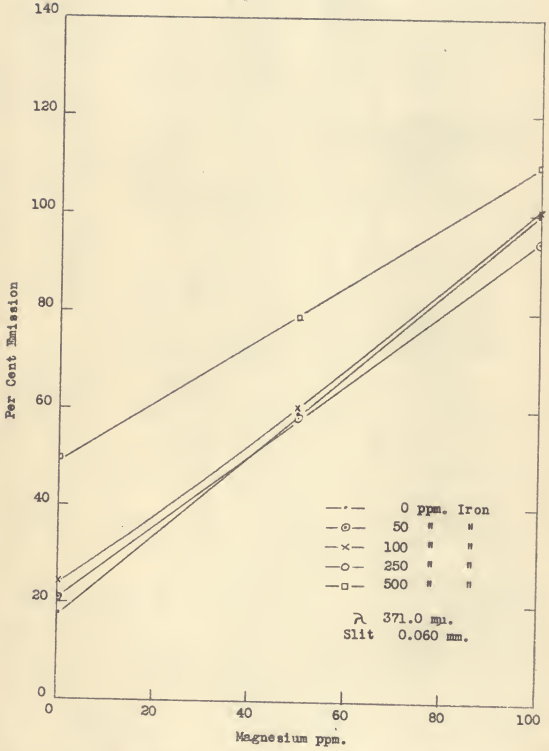

Fig. 9. The Effect of Iron Ion on the Magnesium Flame Emission at the 371.0 mμ. Wavelength.

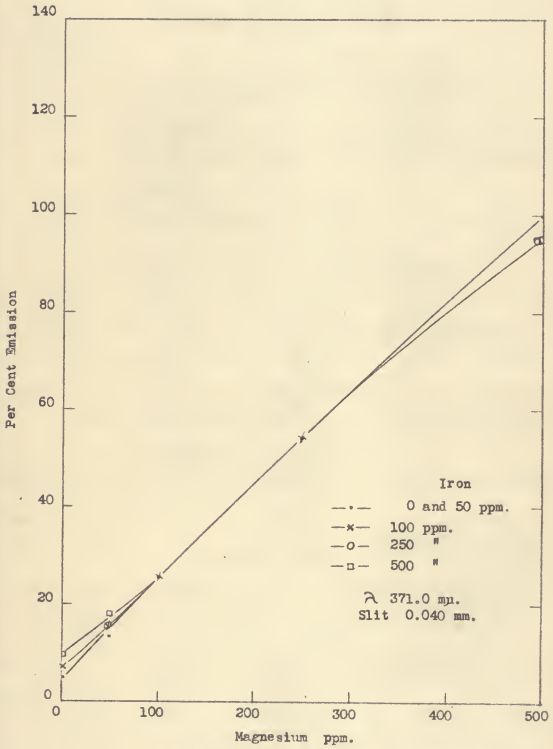

Fig. 10. The Effect of Iron on the Magnesium Flame Emission at the 371.0 mμ. Wavelength.

oxide to produce a slight background effect. Where the solution contained 100 ppm magnesium and 50 ppm iron, the energy available in the flame was divided between the activation of magnesium and iron oxides. Iron oxides (FeO and Fe_2O_3) have very high melting points. Ferrous oxide melts at 1420° C and Fe_2O_3 at 1538° C, which is higher than for elemental iron. This accounts for the depressing effect of 50 ppm iron on the 100 ppm magnesium solution. When the concentration of iron was equal to the highest magnesium standard, the background produced by the iron was increased to about 102 per cent emission. The background at the lower end of this curve was increased about four per cent. The 500 ppm iron produced a serious background effect which was four times as great at the lower end of the curve as compared to the upper end. At the lower end it is all background effect while at the upper end radiation effects predominated which had a tendency to depress the magnesium flame and reduced the background substantially.

This explanation is verified in Figure 10. At the lower end of the curve, all curves containing iron are enhanced and at the upper end all are depressed.

The same type of effect described above was also found at the 383.0 millimicron wavelength; however, the effect due to iron was much greater, as shown in Figures 11

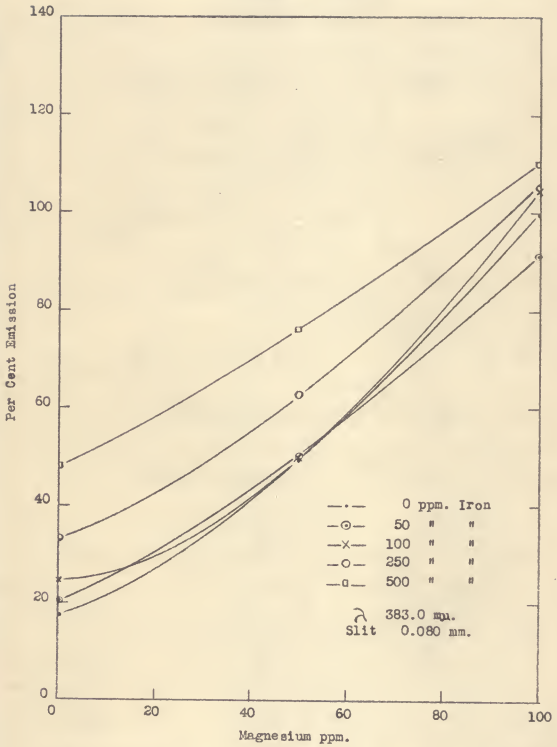

Fig. 11. The Effect of the Iron Ion on the Magnesium Flame Emission at the 383.0 mμ. Wavelength.

and 12. The explanation already given applies here.

Figure 13 shows the effect of iron on the determination of magnesium at the 285.2 millimicron wavelength. No effect of iron was found at concentrations up to 100 ppm; however, the 250 and 500 ppm iron solutions produced a significant depressing effect. Since the background is completely eliminated by using the 285.2 millimicron wavelength and a depressing effect is the only one observed, the above mentioned explanation of the cause of the iron effect is substantiated.

When the magnesium concentration was increased relative to the increase in iron concentration, the interference was not nearly as pronounced as shown by comparing Figure 14 with Figure 13. It is interesting to note that there was no effect due to iron until the concentrations of magnesium exceeded 100 ppm.

The Effect of Sodium on the Magnesium Flame.--The sodium ion enhances the magnesium flame at the 371.0 millimicron wavelength and the magnitude of the enhancement is proportional to the concentration of sodium present in the solution as shown in Figure 15. The solutions containing no magnesium but increasing concentrations of sodium were enhanced more than the solutions containing 100 ppm magnesium with the same concentrations of sodium. The

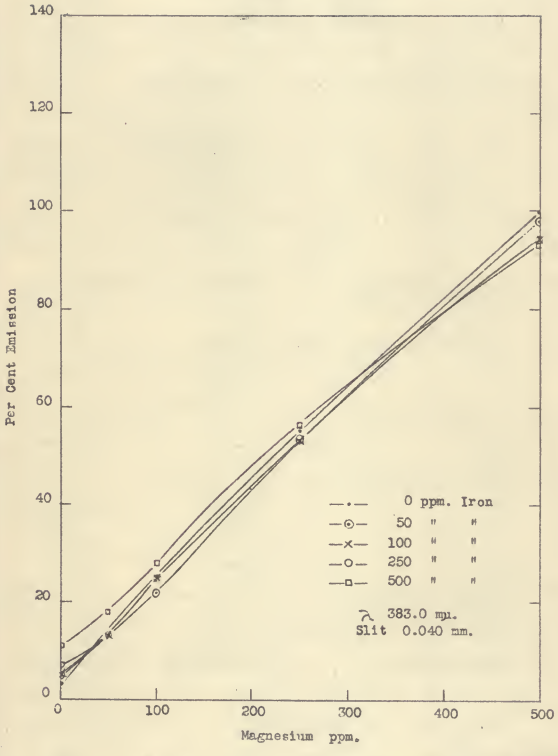

Fig. 12. The Effect of the Iron Ion on the Magnesium Flame Emission at the 383.0 mμ. Wavelength.

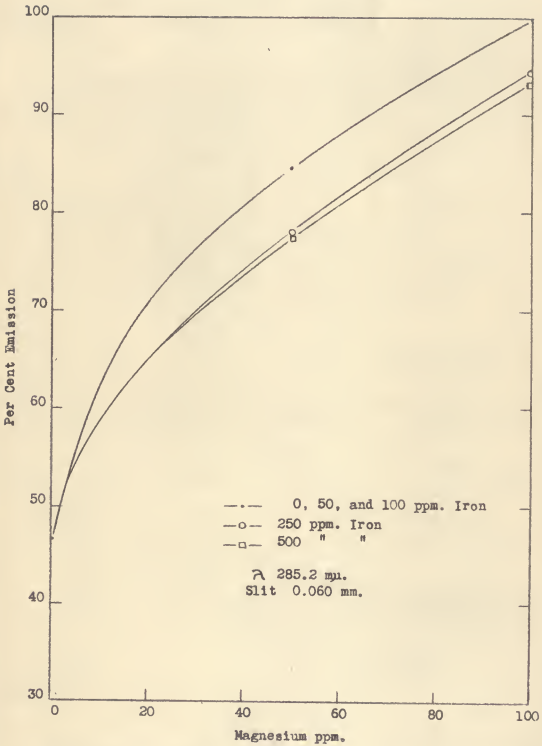

Fig. 13. The Effect of the Iron Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

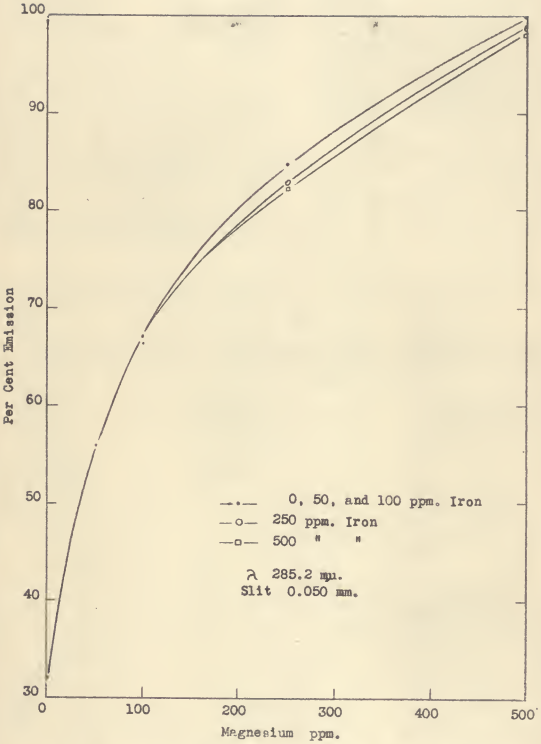

Fig. 14. The Effect of the Iron Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

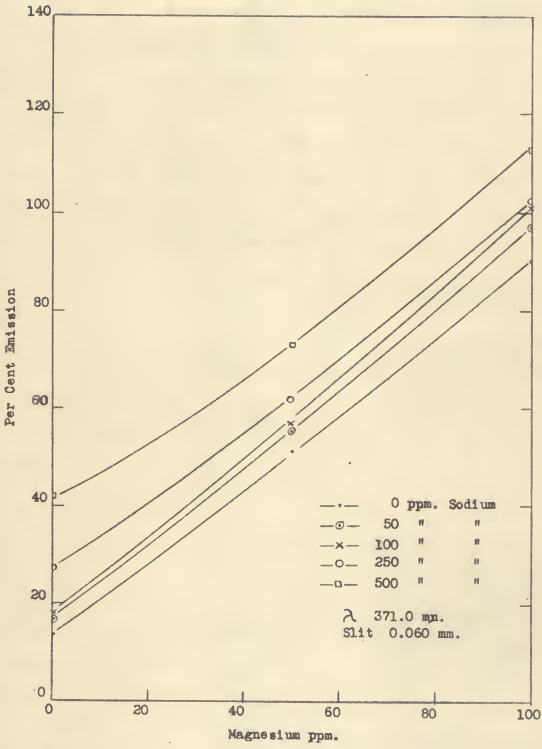

Fig. 15. The Effect of the Sodium Ion on the Magnesium Flame Emission at the 371.0mμ. Wavelength.

background, due to the sodium ion, increases as the magnesium concentration is decreased and the sodium concentration increased. This is clearly shown in Figure 16.

When the same solutions were determined at the 383.0 millimicron wavelength the enhancement due to the sodium produced background was observed again; however, here a greater magnitude was observed, as shown in Figure 17. The enhancement at this wavelength is not nearly so great when the magnesium concentration is increased, Figure 18.

Using the same solutions and the 285.2 millimicron wavelength, no effect due to sodium at any of the concentrations was observed. There was no effect even when the sodium concentration was 500 times greater than the magnesium concentration as shown in Figures 20 and 21.

In view of the above effects produced by the extraneous ions studied at the 371.0 and 383.0 millimicron wavelengths and the absence of any effect of the ions studied so far at the 285.2 millimicron wavelength, it was decided to do the rest of the work at this wavelength. The background, due to other ions, would have to be contended with at both the 371.0 and the 383.0 millimicron wavelengths.

The 285.2 millimicron wavelength is practically free of any background effect and this alone justifies its use over the other two.

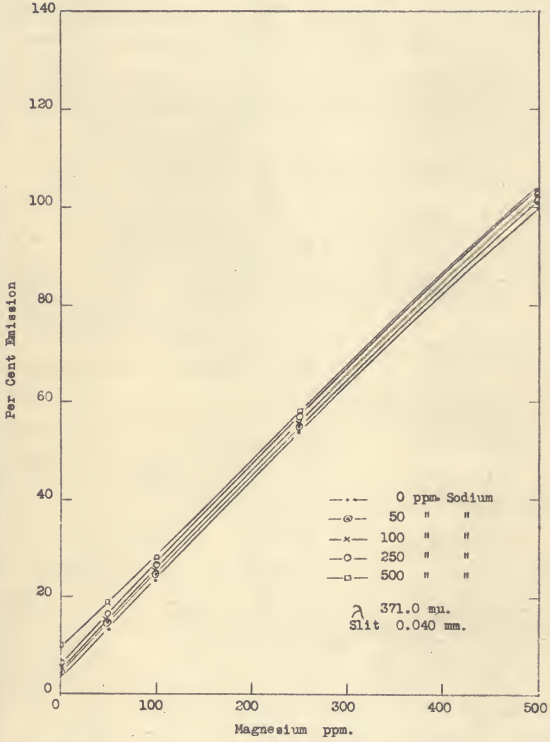

Fig. 16. The Effect of the Sodium Ion on the Magnesium Flame Emission at the 371.0 mu. Wavelength.

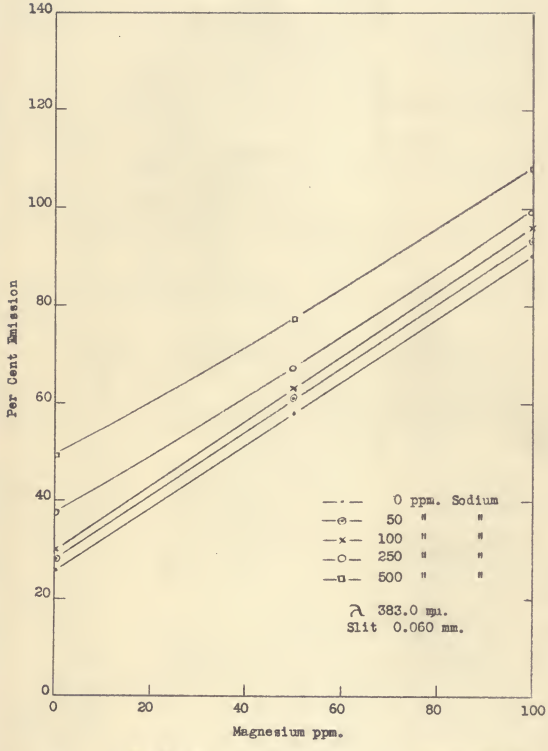

Fig. 17. The Effect of the Sodium Ion on the Magnesium Flame Emission at the 383.0 mμ. Wavelength.

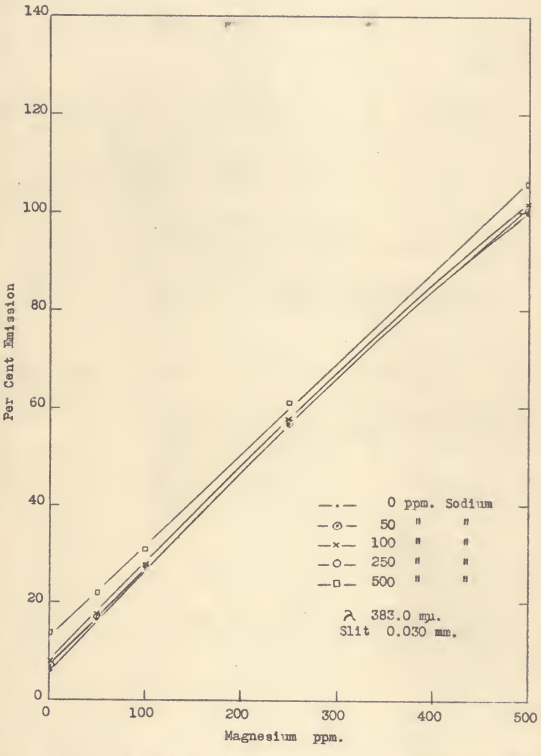

Fig. 18. The Effect of the Sodium Ion on the Magnesium Flame Emission at the 383.0 mμ. Wavelength.

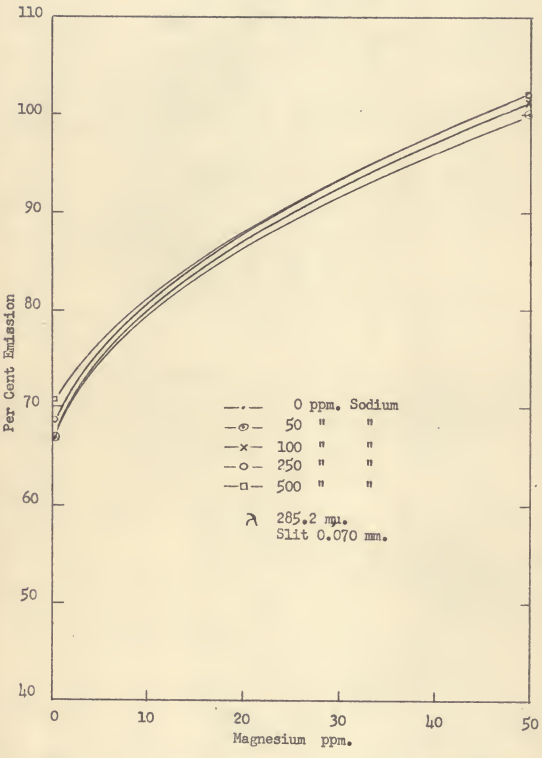

Fig. 19. The Effect of the Sodium Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

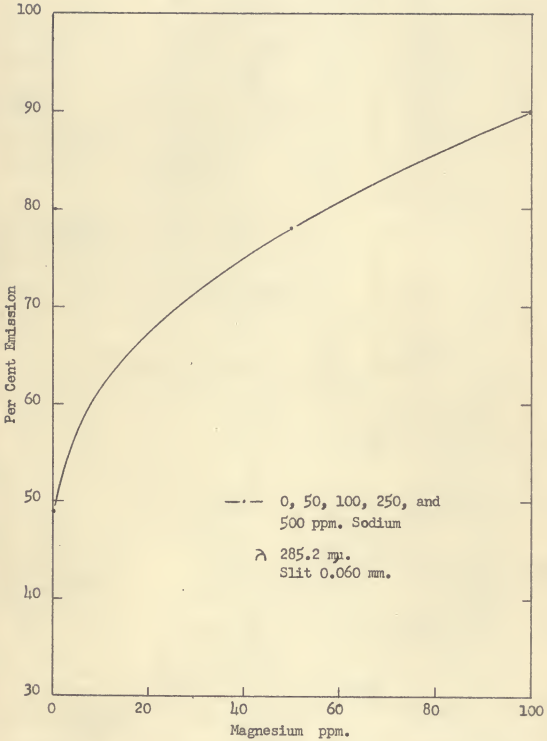

Fig. 20. The Effect of the Sodium Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

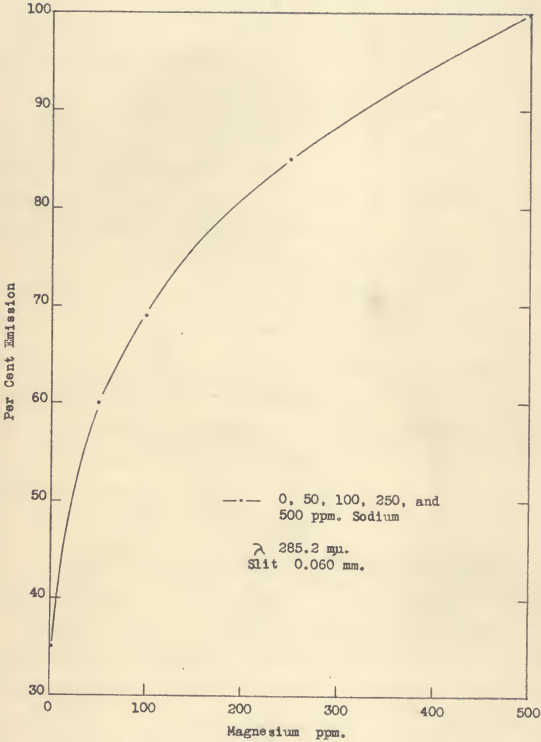

Fig. 21. The Effect of the Sodium Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

The Effect of Sulfur on the Magnesium Flame.--The 285.2 millimicron wavelength is not completely free from the effect of other ions. Figure 22 reveals what happens when sulfur is added as a possible interfering ion to the magnesium solutions. The 50 ppm concentration of sulfur produced an eight per cent depression and the 100 ppm a 14 per cent depression. All concentrations above 100 ppm produced no significant depressing effect even when the concentration was as high as 500 ppm. The use of radiation buffers is based on this fact. By adding 500 ppm sulfur to the standards and the unknowns, the small amount of sulfur present in the unknowns would not produce any added depression over that produced by the buffer.

The best and most logical way of removing the interference is by removing the ion that is causing it. This was attempted by using Dowex 1 anion exchange resin to effect the separation and the results are presented in Figure 23. The resin was practically 100 per cent effective in removing the sulfur from the magnesium solutions. The standard curve containing no sulfur was about four per cent higher than the same standard that was passed through the resin. This indicated that the resin was also retaining a small amount of the magnesium. This was repeated several times and the greatest difference found was four per cent. Most of the time the difference was about one per cent.

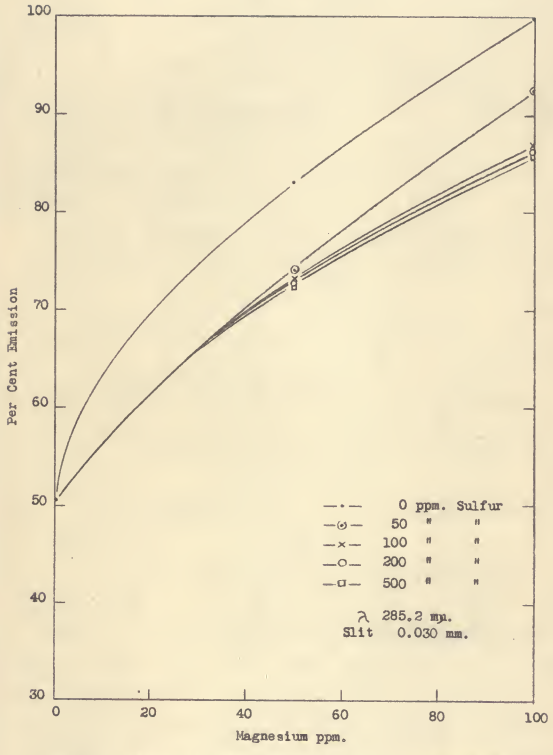

Fig. 22. The Effect of the Sulfate Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

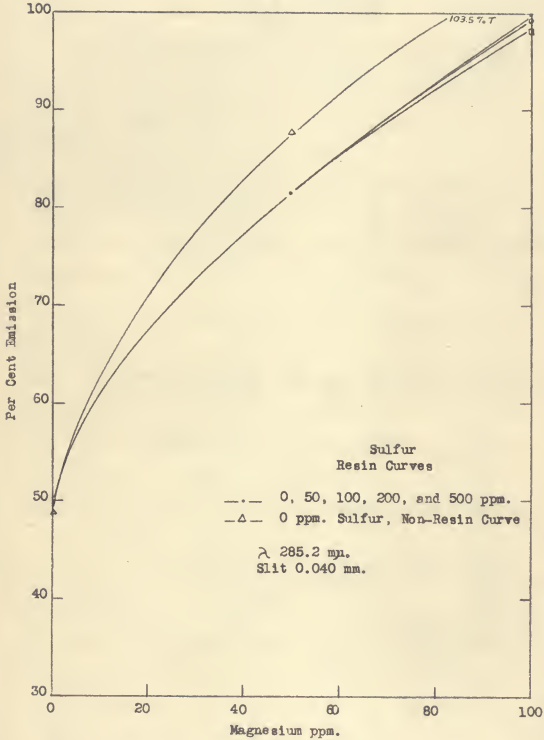

Fig. 23. The Effect of the Sulfate Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength after the Solutions Had Passed Through Resin Columns.

This effect is nullified when determining unknowns, by running the standards used in comparing these unknowns through similar columns of resin.

Figure 24 presents the results that were obtained when the magnesium concentration was increased to 500 ppm. Here the effect was a depression directly proportional to the sulfur concentration. These two figures strongly suggest that when magnesium is present in low concentration, in comparison to sulfur, a chemical combination takes place. The magnesium flame emission is suppressed to the point where there is no magnesium to combine with the sulfur, therefore, the excess sulfur has no further depressing effect. This is emphasized in Figure 24 where the magnesium concentration was increased to equal that of sulfur and the depression was still downward. If the paths of the magnesium curves containing 100, 250 and 500 ppm sulfur are followed it is obvious that they are one and the same line up to 50 ppm magnesium. At the 50 ppm magnesium point, the 250 ppm sulfur curve begins to lag, however, the 500 ppm sulfur is still the same line until the 100 ppm magnesium concentration is reached and then it begins to lag. This is very strongly indicative of a definite chemical combination. When a solution of sulfuric acid is added to the magnesium chloride standards, magnesium sulfate is formed. The melting point of magnesium sulfate is very high (1185° C)

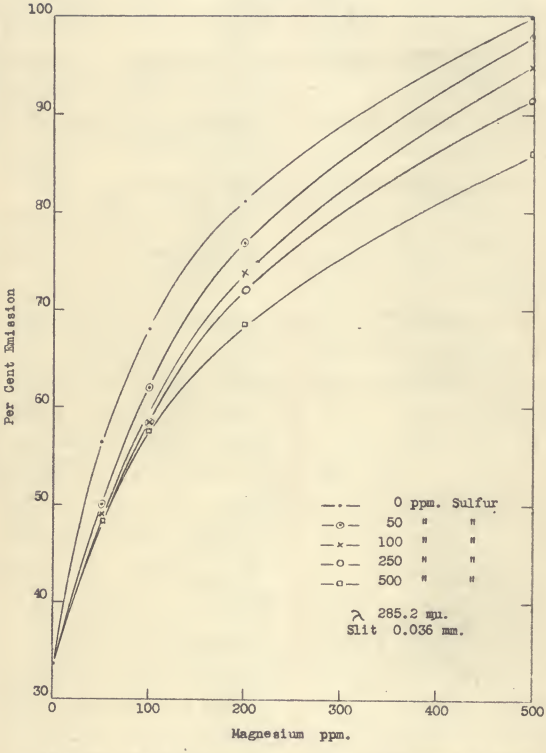

Fig. 24. The Effect of the Sulfur Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

in comparison to magnesium chloride (712° C). When the melting point of the compound formed is high, the interference is also large. The bond between magnesium and sulfate is very strong and its dissociation very slow in the flame.

The results obtained after passing the solutions discussed in Figure 24 through the resin columns are shown in Figure 25. The removal was complete and here the loss of magnesium in the resin was insignificant.

The effect of higher concentrations of sulfur on the magnesium flame emission has been pointed out. Figure 26 shows the effect of lower concentrations of sulfur that would be encountered in most soil dilutions.

The Effect of Phosphorus on the Magnesium Flame.--The addition of phosphorus to the magnesium standards produced a major depressing effect on the magnesium flame. The magnitude of the depression being proportional to the concentration of phosphorus contained in these solutions. In a few plants and in some soils the phosphorus content exceeds the magnesium content. The error resulting from a solution that contained about the same concentrations of both of these elements is obvious by examination of Figure 27. Soil or plant analyses for total magnesium would be of limited value if determined using the flame without prior removal of

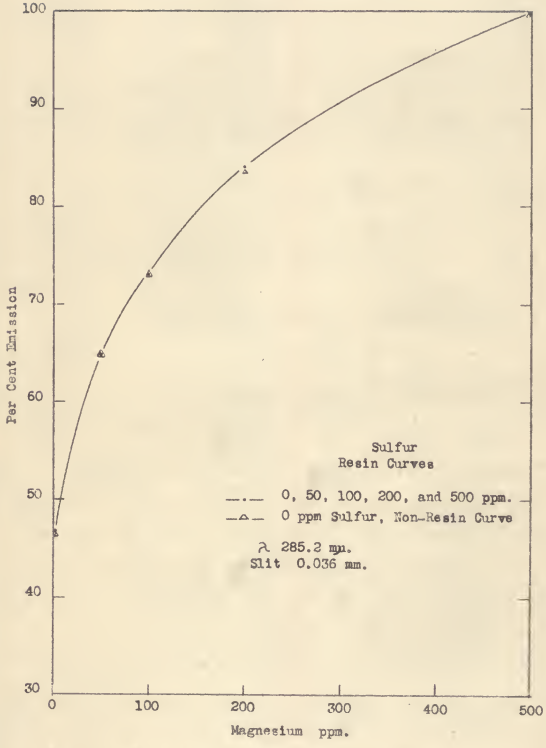

Fig. 25. The Effect of the Sulfate Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength after the Solutions Had Passed Through Resin Columns.

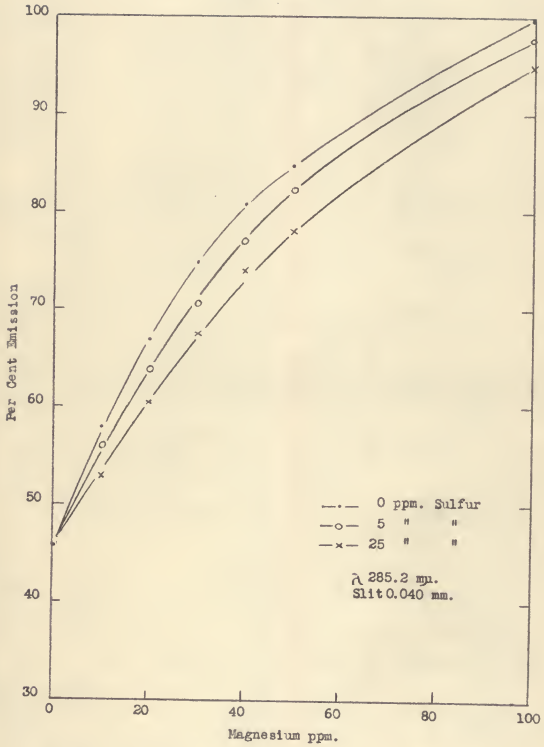

Fig. 26. The Effect of the Sulfur Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength Using Lower Concentrations of Sulfur.

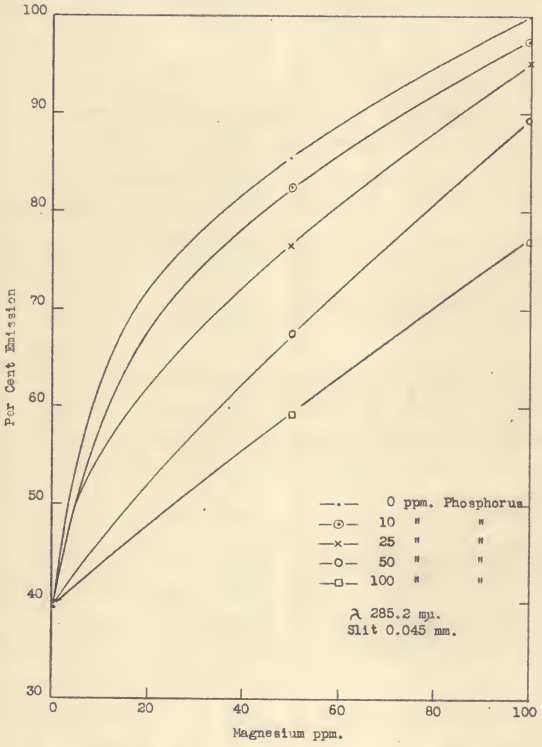

Fig. 27. The Effect of the Phosphorus Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

phosphorus and sulfur or in some way compensating for their presence.

The removal of the phosphate ion in these solutions by the resin was 100 per cent. The resin in this case retained practically no magnesium as shown by the two curves in Figure 28. When the magnesium concentration is increased, the effect of the same concentrations of added phosphorus produced less depression on the magnesium flame as shown in Figure 29.

Figure 30 shows the results of passing the same solutions discussed above through the resin. Again the removal was complete with little difference being noticed between the no phosphorus standards that were passed through the resin as compared to the same ones that were not passed through the resin.

The Effect of Calcium on the Magnesium Flame.--The magnesium flame emission was enhanced only slightly by the additions of calcium up to 500 ppm in the solutions as shown in Figure 31. When the highest concentration of magnesium was 500 ppm, calcium had no effect until its concentration was also increased to 500 ppm in solution as shown in Figure 32. By using higher standards and using the lower portion of the curve the effect of calcium interference was practically eliminated. This is an example of a radiation interference.

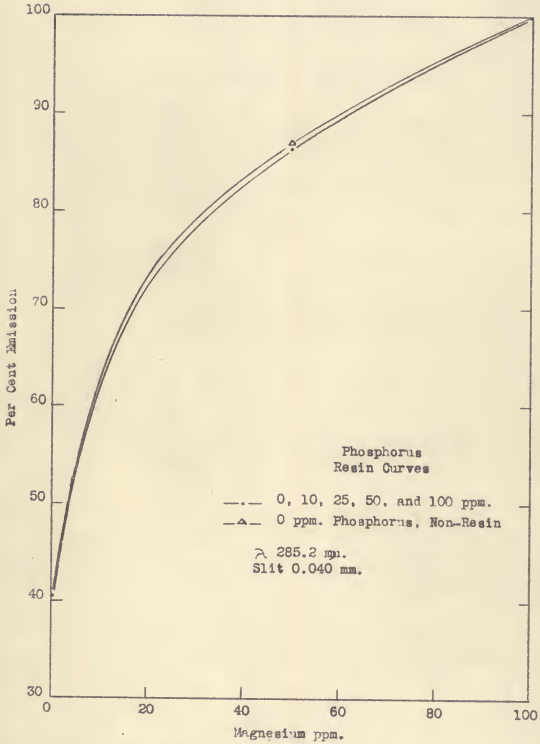

Fig. 28. The Effect of the Phosphorus Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength after the Solutions Had Passed Through Resin Columns.

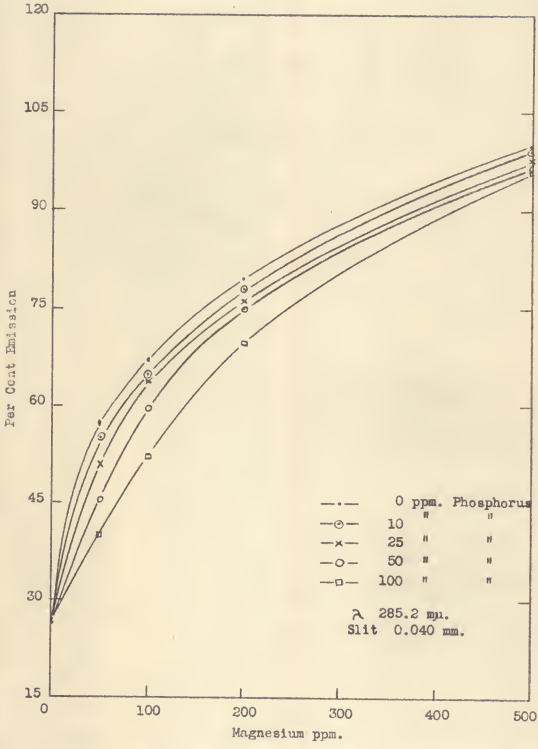

Fig. 29. The Effect of the Phosphorus Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

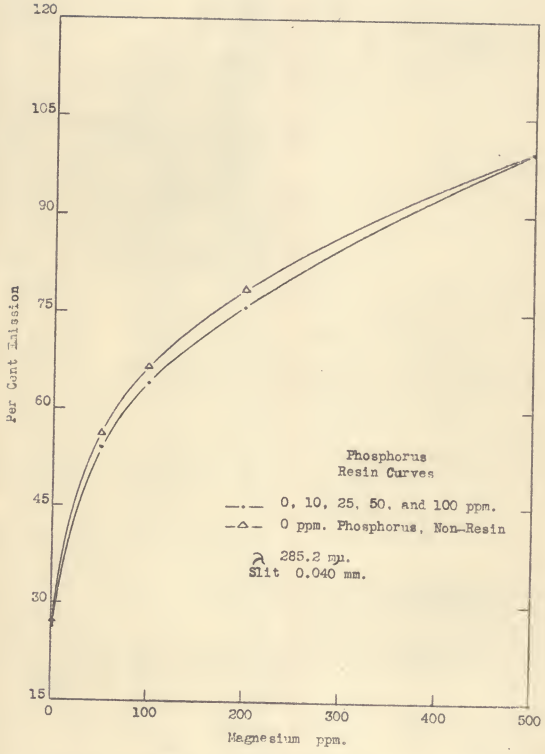

Fig. 30. The Effect of the Phosphorus Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength after the Solutions Had Passed Through Resin Columns.

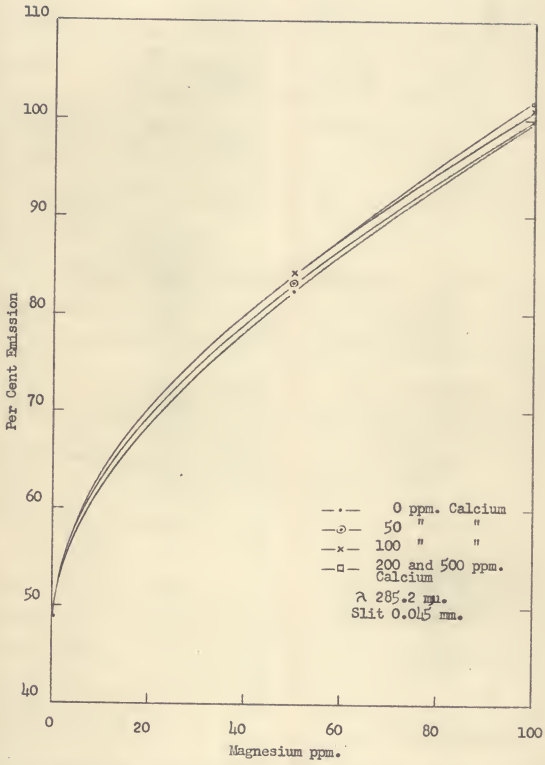

Fig. 31. The Effect of the Calcium Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

The Effect of Manganese on the Magnesium Flame.--Concentrations of manganese up to 50 ppm in solution had no effect on the magnesium flame emission as shown in Figure 33. In Figure 34, where the concentration of magnesium was increased to 500 ppm, it will be observed that there was no effect up to 50 ppm manganese which was the highest concentration tested.

The Effect of Copper on the Magnesium Flame.--Figures 35 and 36 show that concentrations up to 50 ppm copper had no effect on either the 100 or 500 ppm standard.

The Effect of Hydrochloric Acid on the Magnesium Flame.--The effect of increasing molar concentrations of hydrochloric acid on the magnesium flame is shown in Figures 37 and 38. There was no effect of hydrochloric acid on the magnesium flame at any concentration of magnesium until the concentration of the hydrochloric acid exceeded 1.0 molar. The 2.0 molar concentration produced a more pronounced effect when the magnesium concentration was 100 ppm than when it was 500 ppm.

The Effect of Aluminum on the Magnesium Flame.--The presence of aluminum in the magnesium solutions entering the flame depresses the magnesium flame, as shown in Figure 39. The magnitude of this depression being proportional to the

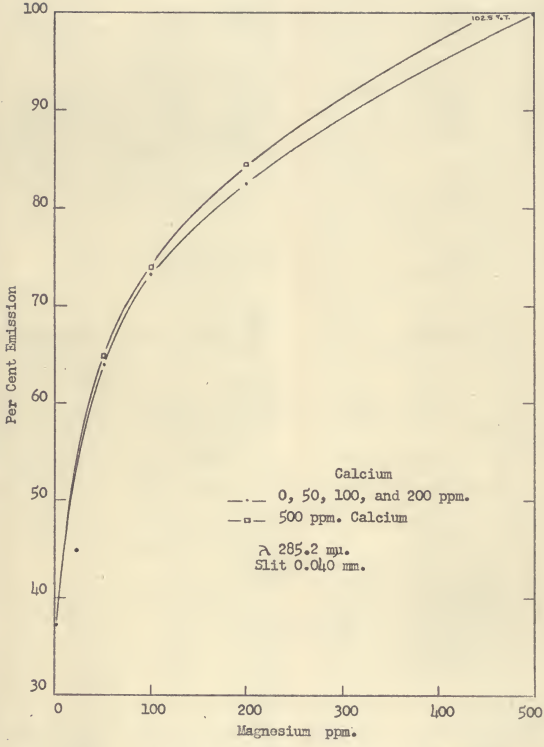

Fig. 32. The Effect of the Calcium Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

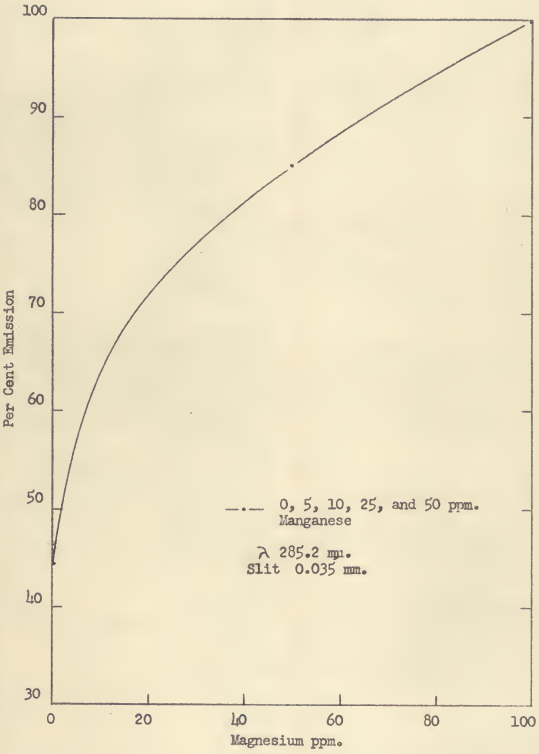

Fig. 33. The Effect of the Manganese Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

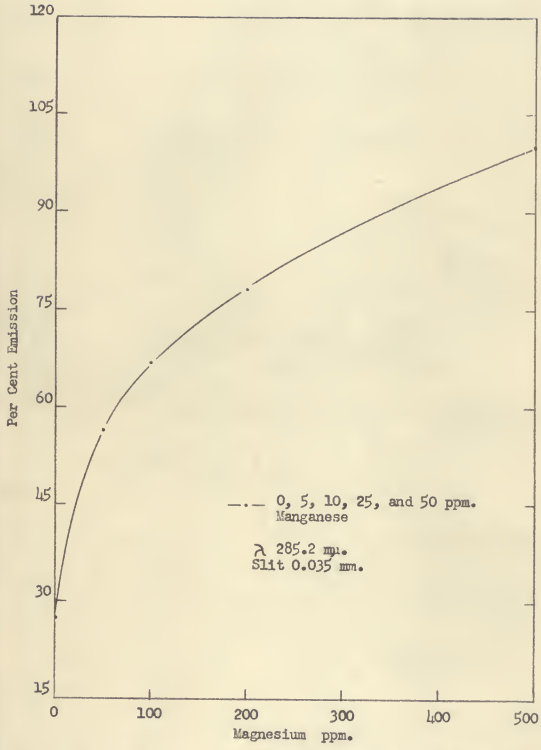

Fig. 34. The Effect of the Manganese Ion on the Magnesium Flame Emission at the 285.2mμ. Wavelength.

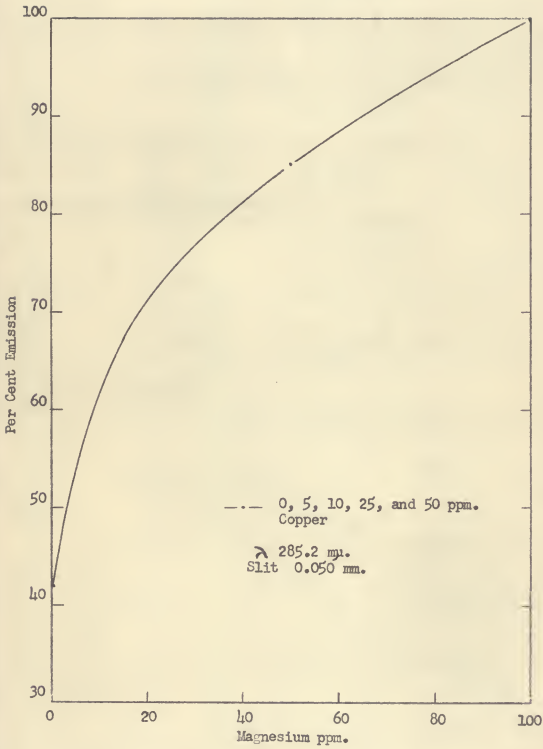

Fig. 35. The Effect of the Copper Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

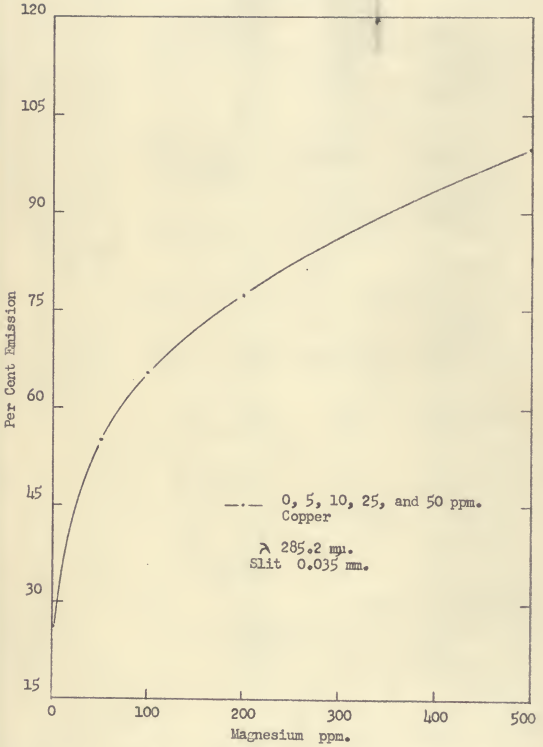

Fig. 36. The Effect of the Copper Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

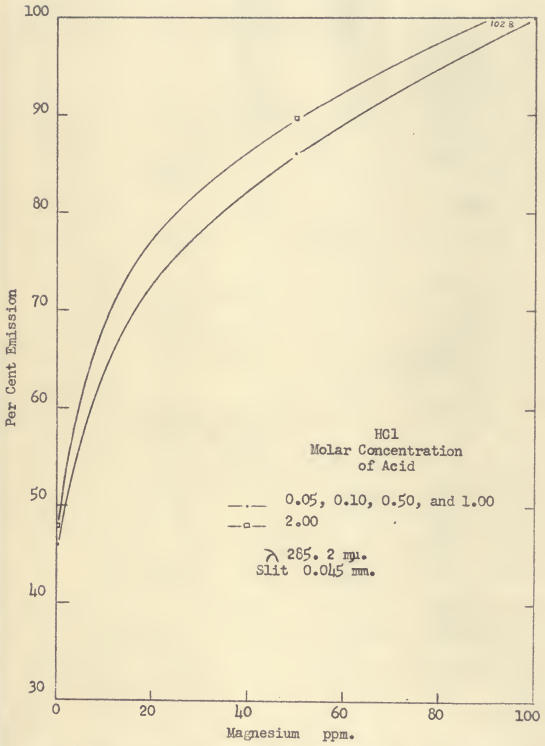

Fig. 37. The Effect of Increasing Concentrations of Hydrochloric Acid on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

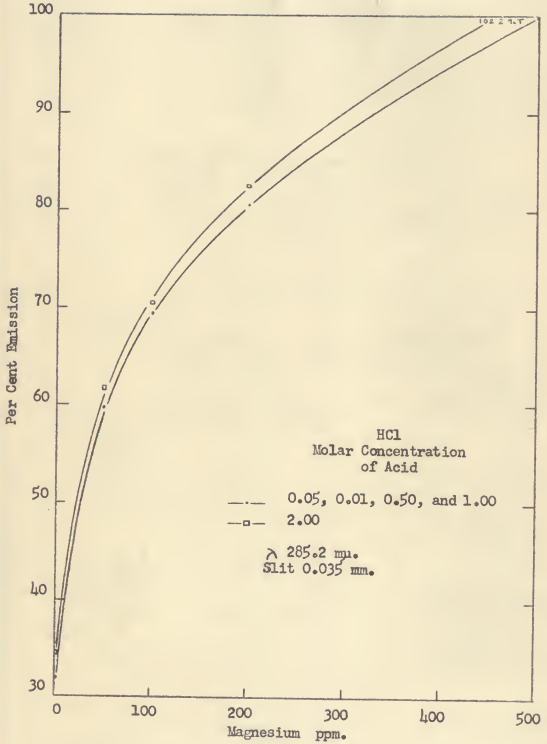

Fig. 38. The Effect of Increasing Concentrations of Hydrochloric Acid on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

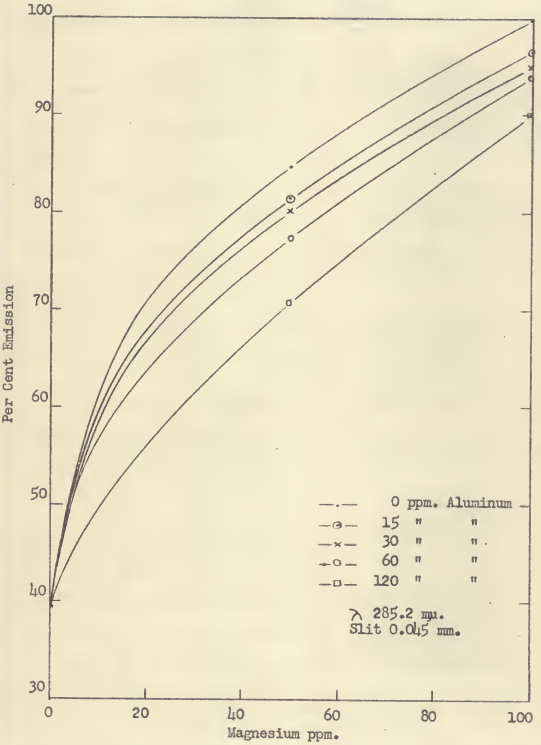

Fig. 39. The Effect of the Aluminum Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

concentrations of aluminum present. Magnesium aluminate has an unusually high melting point (2135° C) and the formation of this compound in the solution or at any time after the solution hits the flame would explain this depressing effect.

From Figure 40, it is obvious that the effect shown due to aluminum is not nearly as great when the magnesium concentration was increased to 500 ppm. Higher concentrations of aluminum were tested with results shown in Figures 41 and 42. The higher concentrations produced greater depressing effects with no tendency toward leveling off.

The Effect of Silicon on the Magnesium Flame.--Silicon added to the magnesium standard solutions produced a greater depressing effect on the magnesium flame than any of the other ions studied. This is demonstrated in Figures 43 and 44. Magnesium silicide is a compound of magnesium having a high melting point (1102° C). Without a single exception, all of the ions found to cause interference in the magnesium determination using the flame, form compounds with magnesium, or the magnesium solvent, that have high melting points. The ions that produced no effect are the ones that form compounds with low melting points. It is very easy to select from the chemical hand book the ions or compounds that will interfere by observing

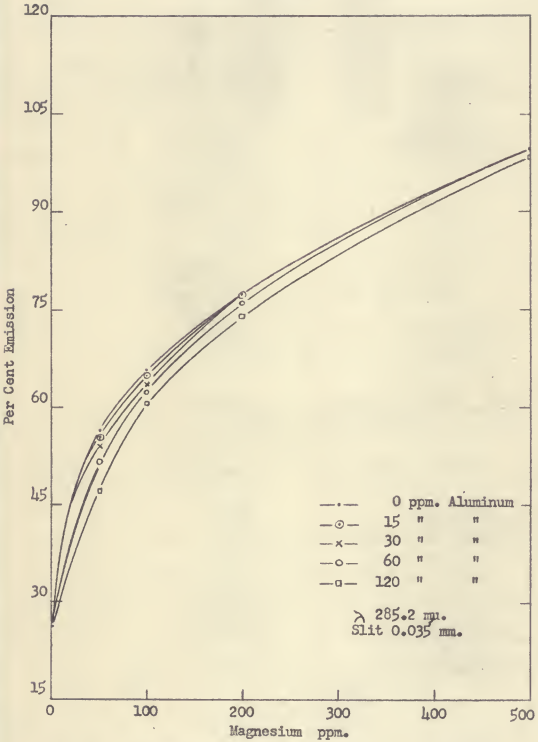

Fig. 40. The Effect of the Aluminum Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

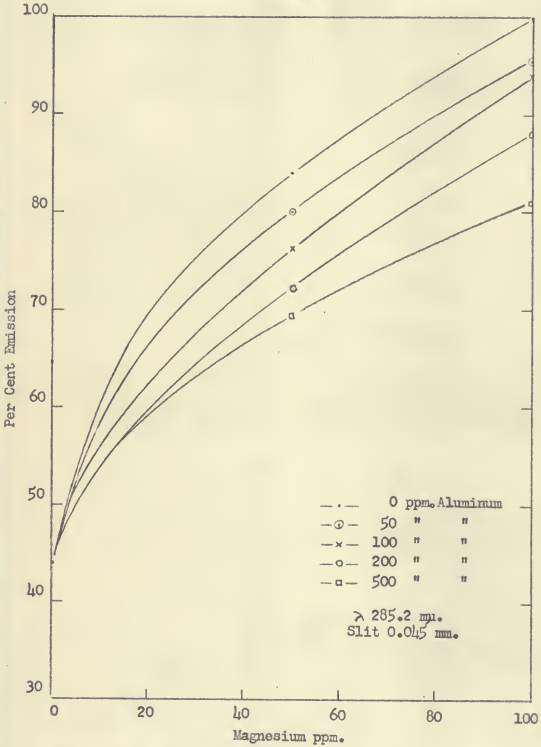

Fig. 41. The Effect of the Aluminum Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength at Higher Concentrations of Aluminum.

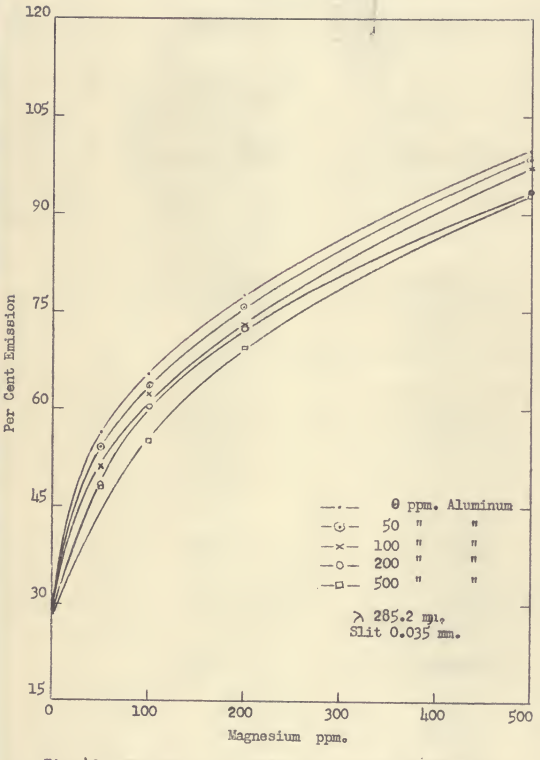

Fig. 42. The Effect of the Aluminum Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength at Higher Concentrations of Aluminum.

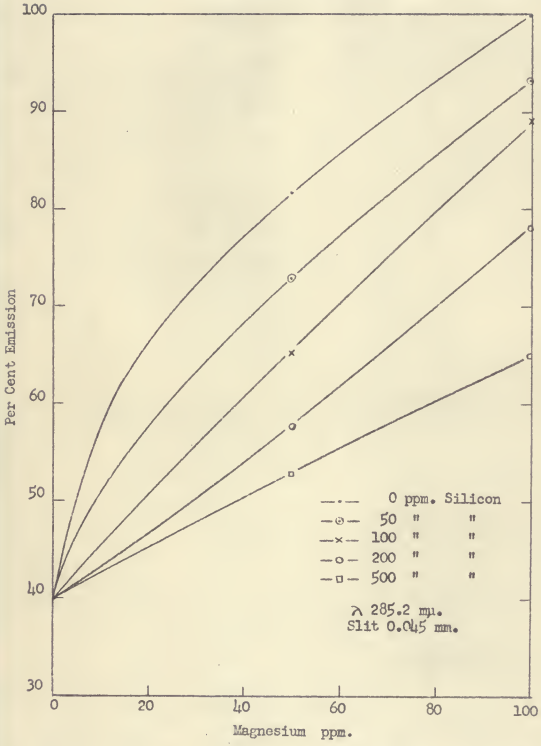

Fig. 43. The Effect of the Silica Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

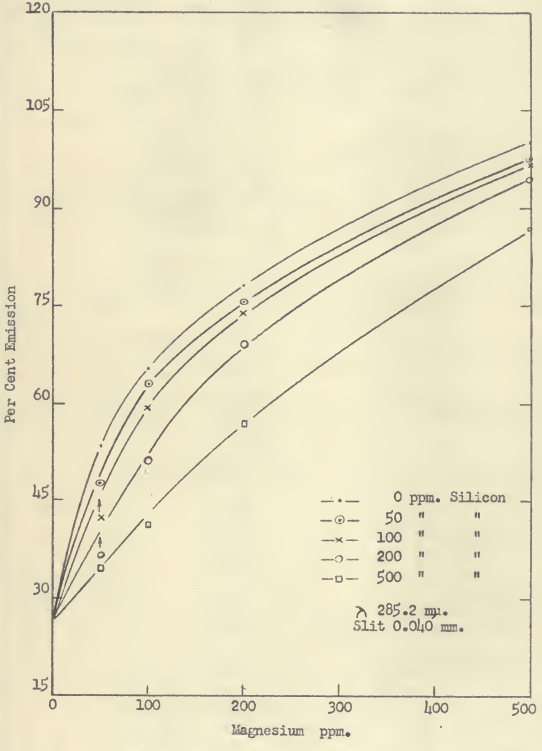

Fig. 44. The Effect of the Silica Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

the melting and boiling points of the compounds formed with the one being determined.

The Effect of Nitrates on the Magnesium Flame.--The absence of any effect due to concentrations of nitrates up to 500 ppm, the highest concentration tested, is shown in Figures 45 and 46. The melting point for magnesium nitrate is 95° C. This is very low in comparison to ions that exhibit a positive effect.

The Effect of Zinc on the Magnesium Flame.--Zinc, like nitrates, had no effect at any of the concentrations tested on the magnesium flame at the 285.2 millimicron wavelength as shown in Figures 48 and 49. Zinc chloride has a melting point of 283° C which is still low, comparatively speaking. The zinc would not be chemically combined with magnesium but could combine with chloride to form zinc chloride.

The Effect of Acetic Acid on the Magnesium Flame.--The presence of acetic acid up to 0.2 molar had no effect on the magnesium flame emission. When the solution was 2.0 molar in acetic acid there was a definite enhancement that was independent of the magnesium concentration as shown in Figures 50 and 51.

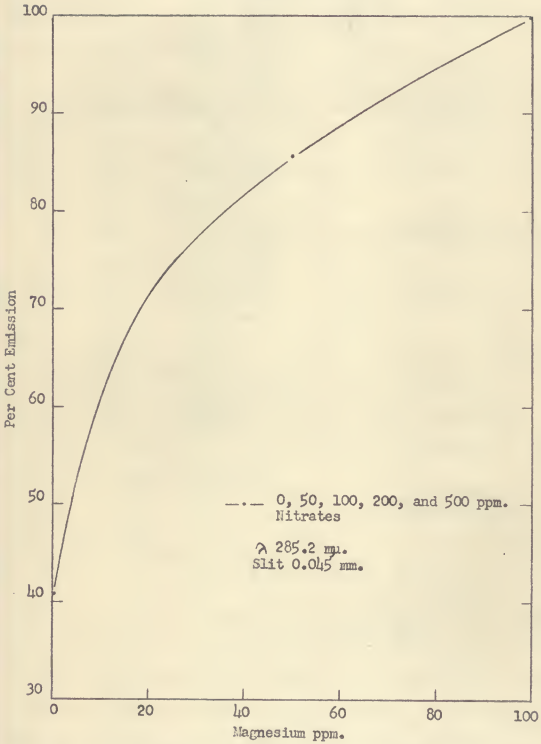

Fig. 45. The Effect of the Nitrate Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

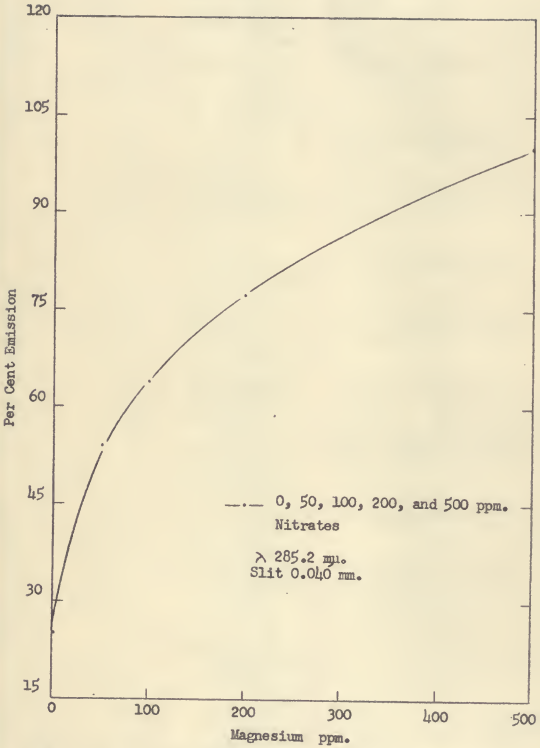

Fig. 46. The Effect of the Nitrate Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

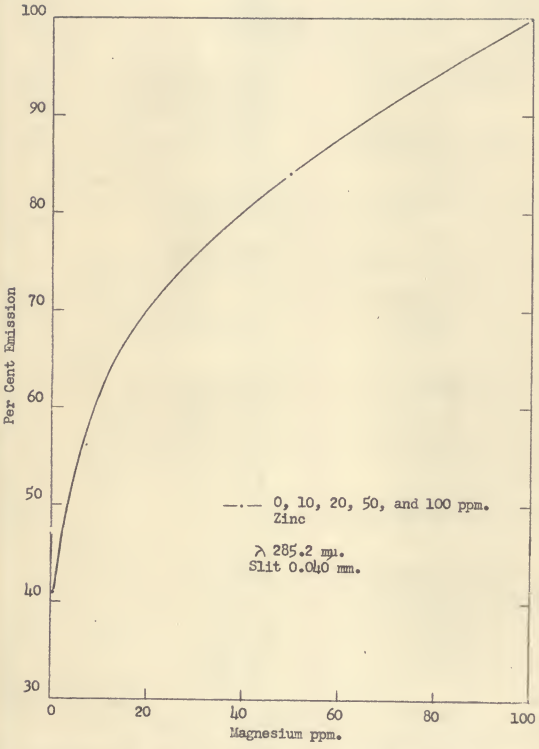

Fig. 47. The Effect of the Zinc Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

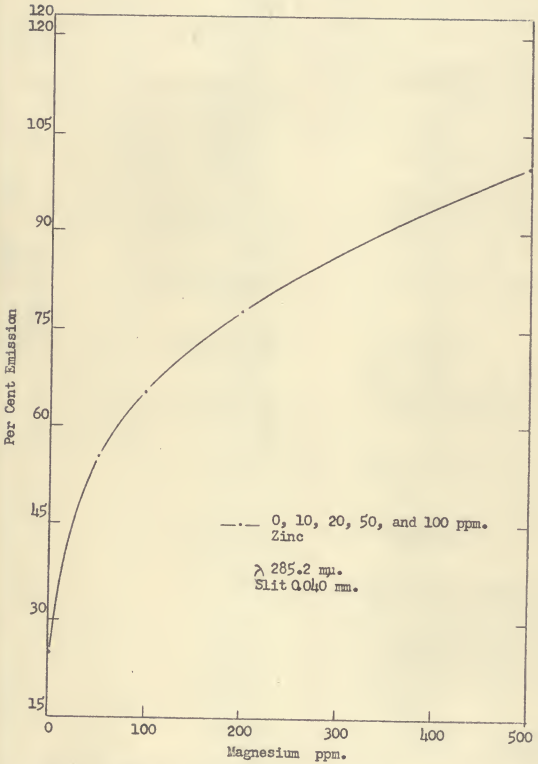

Fig. 48. The Effect of the Zinc Ion on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

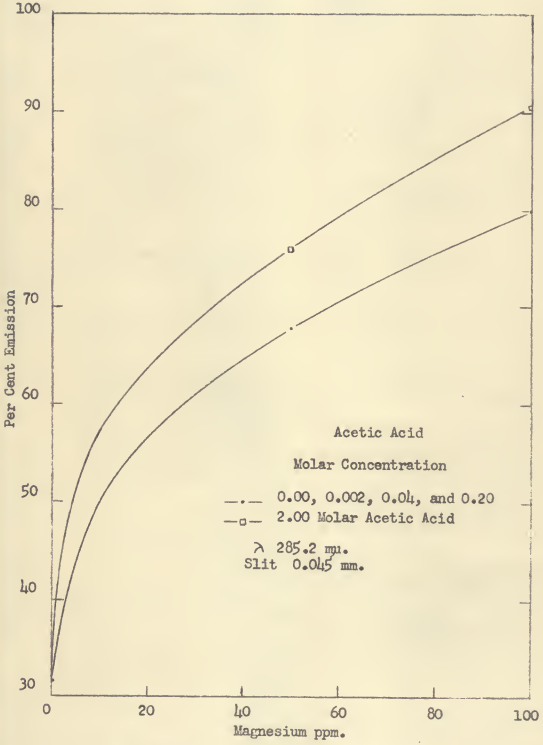

Fig. 49. The Effect of Increasing Concentrations of Acetic Acid on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

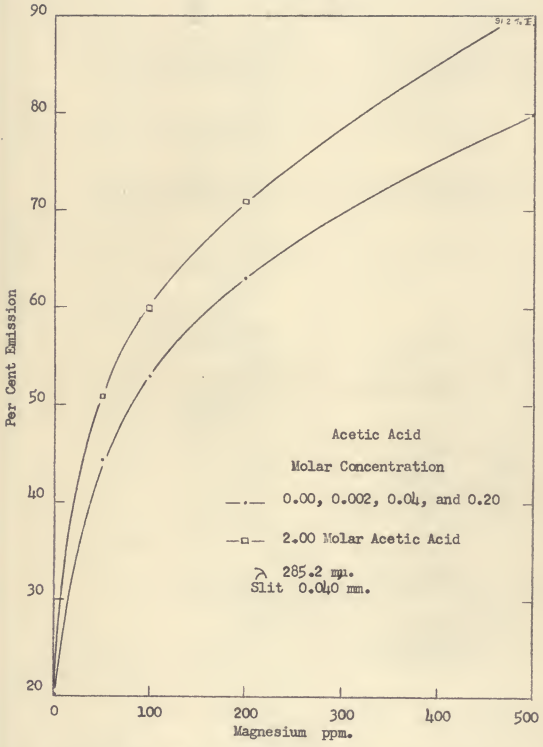

Fig. 50. The Effect of Increasing Concentrations of Acetic Acid on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

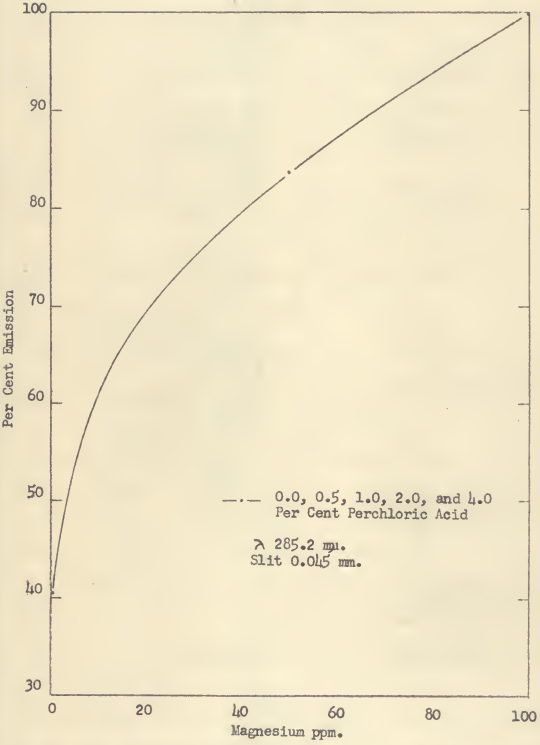

Fig. 51. The Effect of Perchloric Acid on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

The Effect of Perchloric Acid on the Magnesium Flame.--Figure 51 shows the absence of any effect due to perchloric acid up to 4.0 per cent on the 100 ppm magnesium curves. However, Figure 52 indicates that there was an effect on the 500 ppm magnesium curve and it is interesting to note that the enhancement does not begin until after the 100 ppm magnesium point on the curve has been exceeded. The excess chloride ions in the solutions produce the enhancement. Hydrochloric acid did not enhance the magnesium flame until the higher molarities were encountered.

The Effect of Phosphorus and Sulfur Combined on the Magnesium Flame.--Equal concentrations of sulfur and phosphorus were added to the magnesium standard solutions to determine if the depressing effect of each element was additive when the two were combined. Figures 53 and 54 show the results of this experiment. When the two ions are present at lower concentrations, 25 ppm sulfur and 25 ppm phosphorus, the depression due to both ions in the same solution was no greater than the maximum produced by one of the ions alone. When the concentration was 50 ppm for both sulfur and phosphorus, the total depression was 14 per cent. The depression due to sulfur was eight per cent and that due to phosphorus was 11 per cent. It is evident that they are additive to some degree at this concentration; however, the depression due to 100 ppm sulfur was 13 per cent and to

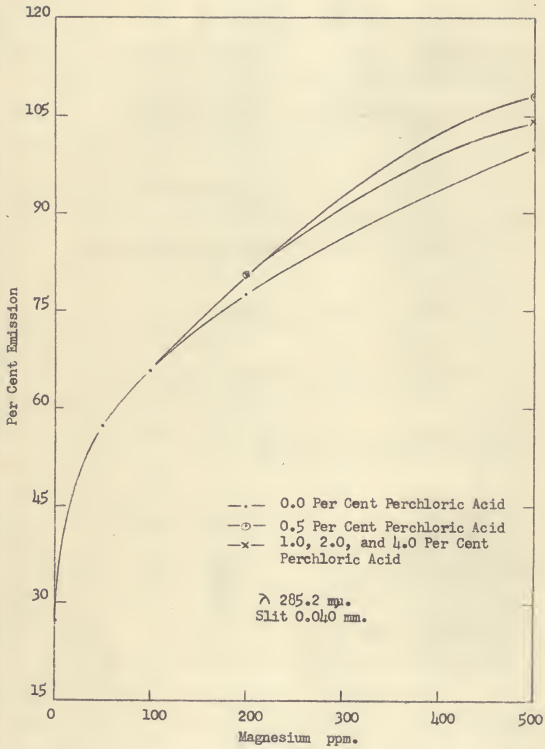

Fig. 52. The Effect of Perchloric Acid on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

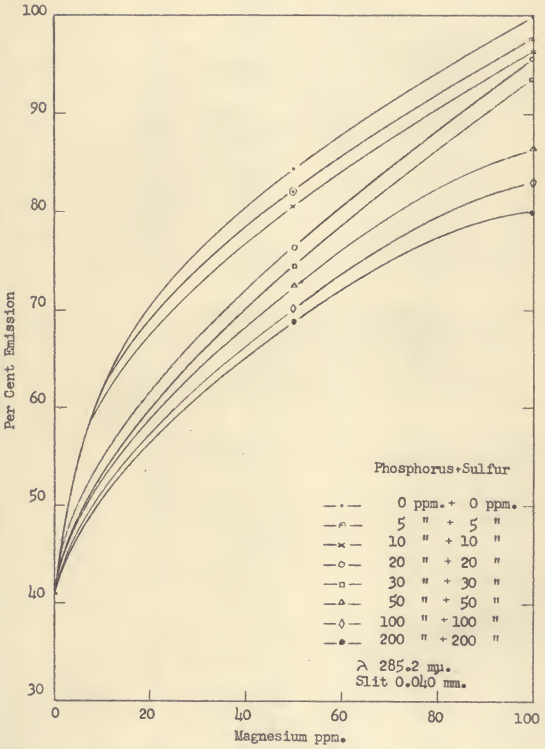

Fig. 53. The Effect of the Phosphorus and Sulfur Ions Combined on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

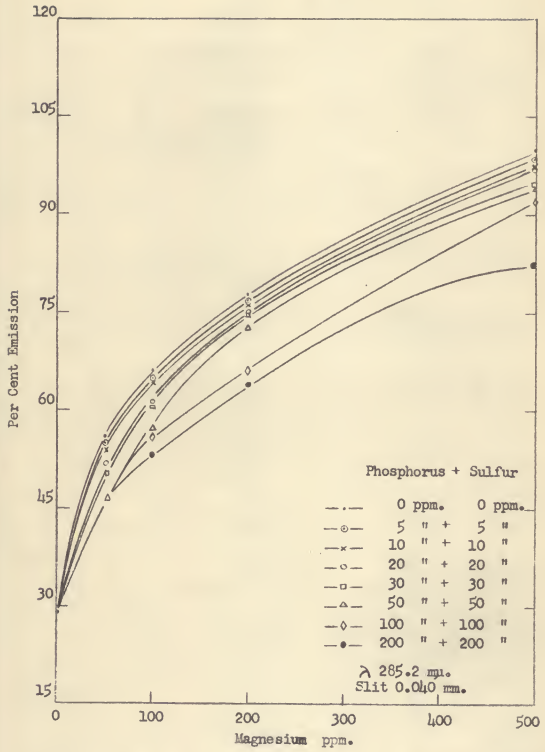

Fig. 54. The Effect of the Phosphorus and Sulfur Ions Combined on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

phosphorus alone was 23 per cent. When the same concentration of the two were combined into one solution the total depression was only 17 per cent. At this concentration the presence of both ions in the same solution produced less effect than the phosphorus alone and more than the sulfur alone. The only conclusion is that these effects are not additive and that the presence of one interfering ion may help reduce the effect of another ion, depending upon the concentration. The depressing effect of both ions collectively is equal to the average value when the ions are considered individually.

The Effect of Iron and Aluminum Combined on the Magnesium Flame.--The same procedure for sulfur and phosphorus as discussed above was followed using iron and aluminum. The results are shown in Figures 55 and 56. The presence of 50 and 100 ppm iron had no effect on the magnesium flame; however, the 50 ppm aluminum depressed the magnesium flame five per cent and the 100 ppm aluminum six per cent. The combined 50 ppm iron and 50 ppm aluminum concentration produced a five per cent depression or the same as the 50 ppm aluminum did alone. The same was true for the 100 ppm combination except the depression was six per cent. The 250 ppm iron concentration depressed the magnesium flame emission six per cent and the 200 ppm aluminum 12 per cent; whereas, the combination of the two

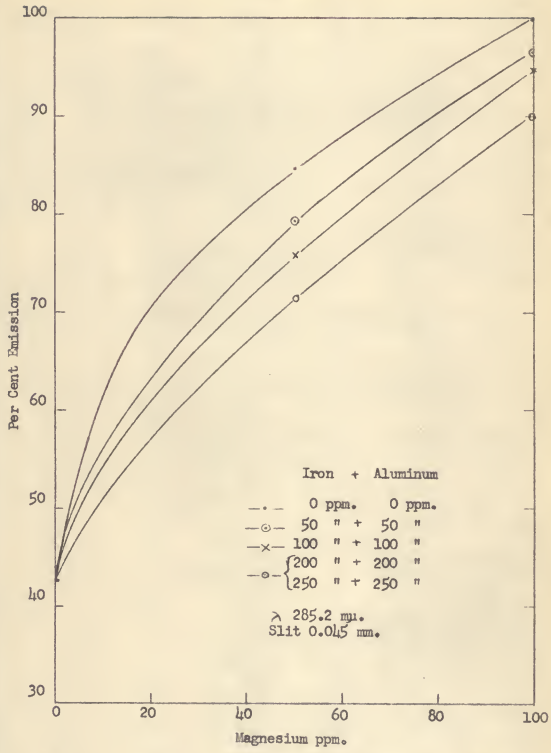

Fig. 55. The Effect of the Iron and Aluminum Ions Combined on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

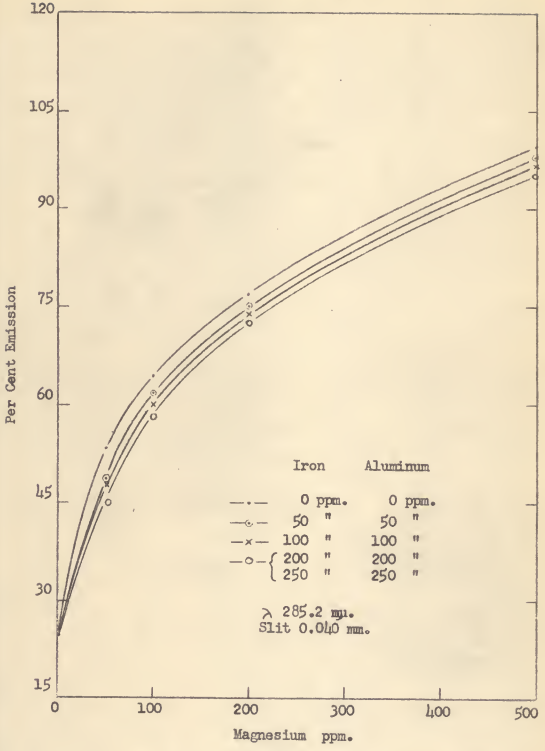

Fig. 56. The Effect of the Iron and Aluminum Ions Combined on the Magnesium Flame Emission at the 285.2 mμ. Wavelength.

produced only a 10 per cent depression. This was the same as was found using the two anions, sulfur and phosphorus. When both were present, the effect seemed to be an average between the two taken individually; therefore, it could not be concluded that 100 ppm phosphorus and 100 ppm sulfur in a solution will produce the same effect as would have been obtained by adding the effect of one to the other mathematically.

No tests were made whereby the two anions and the two cations were combined with magnesium in the same solution. It is reasonable to conclude that a value would have been obtained that would equal the average value of all of the effects taken individually.

Comparison of Methods

Plant Analysis.--The plant material used for making these comparisons was from treated plots already described in this manuscript. Of all the ions tested, silicon, aluminum, iron, phosphorus, and sulfur are the ones which produced interference.

The silica was removed by the dehydration procedure after ashing. In acid solutions, silica is very insoluble; therefore, if the sample has been properly dehydrated and the residue taken up in acid solution, the solution should be free of silica.

Shorland (167) reported that if the ash of a plant contains more than 0.025 per cent aluminum, soil contamination is indicated. This value is probably an upper limit for most plants. Using a one gram sample for ashing, and dissolving the residue in enough 40 per cent hydrochloric acid to give a final dilution of 200 mls. of 0.1 N HCl, the maximum concentration of aluminum would be no greater than one ppm. The effect due to this concentration would not be detected in the flame.

Iron in concentrations up to 100 ppm in solution produced no measurable effect on the magnesium flame. The highest per cent iron reported by Beeson (14) in dry matter of any vegetable, fruit or field crop was 0.483 per cent (4,830 ppm iron). Millet was reported to contain 0.056 per cent iron and oats 0.015 per cent. When the highest concentration listed above is diluted to 200 milliliters, the concentration of iron in this solution would be 24.15 ppm. Solutions of millet ash would contain less than two ppm iron. None of these concentrations are high enough in iron to affect the magnesium flame.

Phosphorus and sulfur were the two remaining ions that had to be eliminated. It is impossible to dilute out the effect of phosphorus or sulfur because most plants contain more phosphorus than magnesium. Many plants contain more sulfur than phosphorus. The effect of phosphorus could

be partially corrected by the use of a phosphorus radiation buffer. This would not work in the case of sulfur because the presence of sulfur produced a pronounced effect on the magnesium flame at all of the concentrations used with no high concentration of sulfur showing any tendency to level off. It was obvious that the only practical method of eliminating the effect of these two ions was by separation. The logical method of separation of these two anions in solution was by the use of an anion exchange resin. Resin separation of the sulfur and phosphorus was then attempted at two dilutions.

Using the 1:100 dilution the resin removed approximately one-half of the phosphorus contained in the two high phosphorus solutions and 70 to 75 per cent of the phosphorus in the low phosphorus solutions in the first four-milliliter aliquot of solution collected after passing through the resin column, Table 6. The calcium values increased as the phosphorus and sulfur were removed. The phosphorus content of the next four-milliliter aliquot of leachate had increased until approximately 90 per cent of the phosphorus found in the original solution was passing through the resin. For each successive four-milliliter sample the phosphorus content increased. The fifth four-milliliter sample contained the same concentration of phosphorus as was present before the solution had passed

TABLE 6

THE PERCENTAGE CALCIUM, MAGNESIUM, AND POTASSIUM DETERMINED ON SUCCESSIVE FOUR MILLILITER LEACHATES COLLECTED AS THE SOLUTIONS PASSED THROUGH THE RESIN AT TWO DIFFERENT DILUTIONS[a]

Sample No.	Non Resin					First 4 mls.				
	Per Cent			ppm		Per Cent			ppm	
	Ca	Mg	K	P	S	Ca	Mg	K	P	S
					1:100 Dilution					
60	0.13	0.19	3.96	32.0	28.0	0.76	0.34	3.92	18.0	0.0
62	0.07	0.16	3.75	34.0	29.0	0.59	0.33	3.65	17.0	0.0
64	0.07	0.10	3.20	20.0	40.0	0.54	0.23	3.03	8.0	0.0
65	0.05	0.16	3.20	20.0	39.0	0.45	0.30	2.85	5.0	0.0
					1:200 Dilution					
60	0.13	0.19	3.96	16.0	14.0	1.15	0.44	4.00	0.0	0.0
62	0.07	0.16	3.75	17.0	14.5	0.96	0.44	3.56	0.2	0.0
64	0.07	0.10	3.20	10.0	20.0	0.80	0.30	3.24	0.0	0.0
65	0.05	0.16	3.20	10.0	19.5	0.66	0.40	3.08	0.0	0.0

[a]Phosphorus and sulfur values reported are ppm P and S in the solution that was passed through the flame.

TABLE 6.--Continued

Sample No.	Second 4 mls.					Third 4 mls.				
	Per Cent			ppm		Per Cent			ppm	
	Ca	Mg	K	P	S	Ca	Mg	K	P	S
					1:100 Dilution					
60	0.46	0.28	4.15	27.0	0.0	0.37	0.23	4.00	30.0	0.0
62	0.28	0.26	3.80	26.0	0.0	0.25	0.19	3.80	31.0	0.0
64	0.27	0.16	3.35	15.0	0.0	0.25	0.13	3.35	18.0	0.0
65	0.22	0.23	3.28	15.0	0.0	0.20	0.18	3.28	18.0	0.0
					1:200 Dilution					
60	0.66	0.35	4.06	0.0	0.0	0.60	0.30	4.06	3.8	0.0
62	0.36	0.34	3.72	0.0	0.0	0.32	0.27	3.73	4.5	0.0
64	0.35	0.22	3.60	0.2	0.0	0.32	0.19	3.60	4.0	0.0
65	0.28	0.28	3.55	0.0	0.0	0.25	0.25	3.55	4.2	0.0

TABLE 6.--Continued

Sample No.	Fourth 4 mls.					Fifth 4 mls.					Sixth 4 mls.				
	Per Cent			ppm		Per Cent			ppm		Per Cent			ppm	
	Ca	Mg	K	P	S	Ca	Mg	K	P	S	Ca	Mg	K	P	S
						1:100 Dilution									
60	0.37	0.23	4.00	31.0	0.0	0.37	0.23	4.00	32.0	0.0					
62	0.25	0.17	3.80	34.0	0.0	0.25	0.17	3.80	34.0	0.0					
64	0.25	0.12	3.28	19.0	0.0	0.25	0.12	3.28	20.0	0.0					
65	0.20	0.17	3.20	20.0	0.0	0.20	0.17	3.20	20.0	0.0					
						1:200 Dilution									
60	0.58	0.30	4.06	9.1	0.0	0.48	0.30	4.06	12.0	0.0	0.37	0.30	4.06	16.0	0.0
62	0.30	0.27	3.73	9.8	0.0	0.25	0.27	3.73	14.0	0.0	0.25	0.27	3.73	17.0	0.0
64	0.31	0.19	3.60	8.0	0.0	0.30	0.19	3.60	10.0	0.0	0.30	0.19	3.60	10.0	0.0
65	0.20	0.25	3.55	9.0	0.0	0.20	0.25	3.55	10.0	0.0	0.20	0.25	3.55	10.0	0.0

through the resin. It is very interesting to note that the calcium concentration in the fifth collection in all of the four samples used is three to four times higher than the same solutions which were not passed through the resin. While the resin was inefficient in removing phosphorus from these sample solutions, it was very efficient in removing the sulfur. This removal of sulfur accounts for the higher values for calcium and magnesium obtained even when much of the phosphorus was not being removed. The potassium values were not significantly changed by the resin treatment.

It was evident from this experiment that the resin was capable of removing at least 17 ppm of phosphorus so the same samples were diluted to give a final dilution of 1:200 that contained 17 ppm phosphorus or a lower concentration and the same experiment repeated. The results of this experiment are shown in Table 6. The first eight milliliters that were collected were found to be free of phosphorus. With this removal of phosphorus the calcium and magnesium values increased accordingly. No phosphorus was found in any of the leachates until after eight milliliters of phosphorus-free solution had been collected.

Table 6 also contains data which indicate that in the first four milliliters of leachate collected the calcium values were unexplainably high. An attempt to isolate this trouble was undertaken. The same experiment

was repeated using one milliliter aliquots of the 1:200 dilution to determine exactly which one was producing the high values. The first milliliter collected was very cloudy in appearance and produced readings that were higher than the highest calcium and magnesium standards used. The second milliliter through the eighth milliliter collected were clear and gave identical values with those reported for the second four milliliters reported in Table 6. It was concluded from this that all of the unknowns would have to be diluted to a point where the phosphorus content did not exceed 17 ppm in the solution that was to be passed through the resin. This experiment also indicated that the first milliliter had to be discarded since it was necessary to wash the resin free of colloidal size particles of resin which produced a significant enhancement to both the calcium and magnesium flame.

A comparison of the flame method for the determination of calcium and magnesium, using the above-described techniques, with the standard chemical procedures was made. The chemical method used for the calcium comparison was the permanganate titration procedure listed in A.O.A.C. (3). The thiazole yellow method using Mehlich's modification (99) was used for the magnesium comparison. These results are reported in Table 7.

TABLE 7

PER CENT CALCIUM AND MAGNESIUM FOUND IN HYDROCHLORIC ACID SOLUBLE PLANT ASH USING DIFFERENT METHODS OF ANALYSES

Sample No.	Calcium			Magnesium		
	Flame No Resin	Flame Resin	AOAC	Flame No Resin	Flame Resin	Thiazol Yellow
P-803-3	0.13	0.55	0.47	0.08	0.09	0.09
4	0.08	0.37	0.33	0.06	0.08	0.08
6	0.10	0.42	0.41	0.07	0.08	0.08
8	0.10	0.44	0.38	0.05	0.08	0.07
10	0.11	0.45	0.41	0.08	0.10	0.10
11	0.11	0.48	2.43	0.06	0.09	0.09
12	0.10	0.44	0.42	0.05	0.08	0.07
14	0.11	0.47	0.39	0.06	0.09	0.09
15	0.10	0.45	0.40	0.06	0.09	0.09
16	0.08	0.33	0.29	0.06	0.10	0.09
18	0.12	0.46	0.46	0.06	0.09	0.09
19	0.11	0.51	0.39	0.06	0.08	0.08
P-743-1	0.13	0.53	0.47	0.16	0.24	0.22
2	0.18	0.56	0.55	0.15	0.20	0.19
3	0.10	0.43	0.38	0.06	0.10	0.10
4	0.12	0.53	0.48	0.08	0.15	0.11
5	0.07	0.32	0.29	0.00[a]	0.00[a]	0.00[a]
6	0.13	0.43	0.42	0.31	0.43	0.43
7	0.13	0.39	0.38	0.33	0.41	0.42
8	0.18	0.51	0.49	0.29	0.39	0.39
9	0.18	0.52	0.52	0.33	0.42	0.39
10	0.12	0.44	0.41	0.28	0.38	0.36
11	0.08	0.38	0.35	0.09	0.11	0.11
12	0.11	0.45	0.42	0.10	0.12	0.10

[a]These are missing values.

The data in Table 7 indicate very close agreement between the flame-resin and thiazol yellow methods. The flame method averaged two and one-half per cent higher than the thiazol yellow method. The resin values are not too much higher than the non-resin values where the magnesium concentration is very low; however, this was not the case when higher magnesium concentrations were found. It was obvious from the interference curves discussed previously that the lower portions of the curves are not as greatly affected by interfering ions as the upper portion. This held true in this experiment where, at the higher magnesium concentrations, greater interference was noted and lower magnesium values were obtained when the resin was not used.

Fair agreement between the two calcium methods was found. The flame values were about eight per cent higher than the chemical method. The concentration of sodium and potassium in these solutions was sufficient to account for the error according to results published by West and False (170). This error does not appear large when compared to that present if the anions are not removed prior to the calcium determination as shown in Table 7.

The final test of the method was made by adding increasing known concentrations of magnesium to several representative acid solutions of plant ash. These solutions were passed through the resin and after discarding the

first milliliter that came through the next four were collected and used for the analyses. The results are reported in Table 8.

The recovery of the added magnesium was very good at both dilutions; however, using the 1:200 dilution the recoveries of added magnesium at the higher concentration were somewhat better than the 1:100 dilution. This is mainly because at the higher dilutions the magnesium values are lower and the lower portion of the curve is less affected by calcium, the only ion remaining that is likely to cause interference.

Soil Analysis.--In addition to sulfur and phosphate ion interference which was discussed under plant analysis for total magnesium and calcium; iron and aluminum also are important in the analysis of soils due to their increased concentration in the ash. The Suwannee Valley soils that were used in the greenhouse and field plots were high in iron and aluminum. The iron and aluminum were removed by precipitation with ammonium hydroxide. The addition of ammonium hydroxide precipitates iron as Fe_2O_3, aluminum as Al_2O_3, and phosphorus as P_2O_5. In one operation three ions that cause most of the interference to the magnesium flame are removed. The resin used in conjunction with the precipitation technique will remove any sulfur that might be present.

TABLE 8

RECOVERIES OF ADDED MAGNESIUM TO FIVE REPRESENTATIVE PLANT ASH SOLUTIONS AT TWO DIFFERENT DILUTIONS USING RESIN TO REMOVE ANIONS

Sample No.	1:200 Dilution					1:100 Dilution				
	Magnesium Added ppm					Magnesium Added ppm				
	0	10	20	30	40	0	10	20	30	40
	Magnesium Found ppm									
1	23.5	33.0	43.2	52.0	64.0	47.0	57.0	66.8	76.0	85.0
2	15.5	25.3	35.0	46.0	65.4	31.0	41.0	50.6	60.0	70.0
3	22.5	32.5	42.0	51.0	66.0	45.0	55.5	64.4	73.3	84.0
4	10.0	19.9	30.3	40.1	50.8	20.0	30.1	40.0	49.4	58.8
5	9.0	19.0	29.2	88.5	49.3	18.0	27.8	37.9	48.3	57.5

An experiment was set up to study the effect of pH on the ammonium hydroxide precipitation of iron, aluminum, and phosphorus as well as to determine what loss of magnesium and calcium, if any, occurred using this technique. The proposed technique is much simpler than the A.O.A.C. method and the recovery of added magnesium was good.

The experiment was carried out using 50 ml. of 10 different acid soluble soil ash solutions combined into one single solution. The one solution was mixed thoroughly and sixteen 25 ml. aliquots were added to 50 ml. volumetric flasks. No magnesium was added to four of these flasks. The remaining 12 flasks in groups of four received 8, 16 and 32 ppm magnesium. Three drops of the indicators listed in Table 9 were used to adjust the solution to the desired pH using dilute (one-half normal) ammonium hydroxide. The precipitate was removed by the use of a centrifuge and the clear supernatant was decanted into 5 ml. flame beakers for the determinations. The results are shown in Table 9.

The magnesium concentration was found to be 7.2 ppm and the calcium concentration 5.0 ppm in the solution prior to adding the ammonium hydroxide. The addition of the ammonium hydroxide did not completely precipitate all of the oxides of iron, aluminum, and phosphorus until the pH was increased to 6.5. The maximum magnesium concentration was determined when the pH was adjusted to 5.5; however, the

TABLE 9

RECOVERIES OF ADDED MAGNESIUM AND CONCENTRATIONS OF CALCIUM AND MAGNESIUM FOUND AFTER USING AMMONIUM HYDROXIDE TO PRECIPITATE THE IRON, ALUMINUM, AND PHOSPHORUS OXIDES AT INCREASING pH LEVELS

Indicator Used	pH	Magnesium Found After Precipitation With Ammonium Hydroxide					
		No Magnesium Added			8 ppm Magnesium Added		
		Ca	Mg	P	Ca	Mg	P
		ppm					
Methyl Orange	4.5	4.8	7.0	20.0	4.8	13.4	20.0
Bromo Cresol Green	5.5	8.9	11.2	3.5	16.3	19.0	0.0
Bromo Thymol Blue	6.5	16.3	11.2	0.0	16.3	19.0	0.0
Phenol Red	7.5	16.3	11.2	0.0	16.3	19.0	0.0
		16 ppm Magnesium Added			32 ppm Magnesium Added		
		Ca	Mg	P	Ca	Mg	P
		ppm					
Methyl Orange	4.5	4.8	21.5	20.0	4.5	42.0	21.0
Bromo Cresol Green	5.5	6.5	26.5	14.0	5.5	44.0	16.0
Bromo Thymol Blue	6.5	16.0	26.5	0.0	16.5	44.0	0.0
Phenol Red	7.5	16.3	26.5	0.0	16.5	44.0	0.0

calcium values increased in two cases until the reaction was increased to pH 6.5.

The recovery of the added magnesium was very good at all of the concentrations used as indicated in Table 9. The above solution was passed through a column of resin after the precipitation and no increase or decrease was found.

Data in Table 10 give a comparison of the resin values to the ammonium hydroxide precipitation values along with the results without either treatment.

The results in Table 10 indicate that no additional magnesium was recovered by use of the resin after the solutions had been treated with ammonium hydroxide. This indicates that the sample either contained only small concentrations of sulfur to begin with or the sulfur was lost during ashing.

Soil and Plant Experiments

Greenhouse.--This experiment was carried out to determine the response of oats to magnesium applied to Jonesville fine sand at six levels. Daily observations were made in order to determine how soon a deficiency would occur. The first deficiency symptom appeared one week after germination. Chlorosis was observed on the three pots without magnesium treatment. All of the others appeared normal

TABLE 10

THE COMPARISON OF FOUR SAMPLES USING AMMONIUM HYDROXIDE AND RESIN TO SEPARATE INTERFERING IONS

Sample No.	Ash Solution No Treatment		Ammonium Hydroxide Precipitation		Ammonium Hydroxide and Resin	
	Magnesium	Phosphrous	Magnesium	Phosphrous	Magnesium	Phosphrous
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
52	8.5	6.6	21.3	0.0	21.3	0.0
53	9.5	5.6	23.8	0.0	23.8	0.0
54	10.0	5.2	21.3	0.0	21.3	0.0
55	9.3	5.1	23.8	0.0	23.8	0.0

at this time. However, six days later, the lower leaves of plants receiving magnesium at the rates of 15 and 30 pounds per acre became chlorotic. Plants growing in pots receiving the higher rates were normal. Plants receiving no magnesium were now showing pronounced deficiency symptoms on all leaves except the two or three youngest leaves and did not grow as rapidly as plants receiving magnesium at any time during the experiment.

Yield.--All of the magnesium treated soils produced more oats than the untreated soils, Table 11. The difference due to the addition of 15 pounds per acre magnesium was not significant at either the five or one per cent level of probability, however, there was a measurable increase in weight of dry matter produced. The increase due to the addition of magnesium equivalent to 30 pounds per acre was significant at the five per cent level and approached significance at the one per cent level of probability. The 60 and 120 pound per acre rate produced yields that were significantly higher than yields from untreated pots. The 240 pound per acre rate was significantly lower than the 120 pound per acre rate; however, it was significantly higher than the yield from the pots receiving no magnesium. In either case the difference was significant at the one per cent level. This indicated that at some concentration

TABLE 11

CHEMICAL COMPOSITION AND YIELDS FROM MAGNESIUM EXPERIMENT IN THE GREENHOUSE

Magnesium Applied	P	Ca	Mg	K	N	Yield
lbs./acre	(%)	(%)	(%)	(%)	(%)	gms/pot
First Cutting - Oats						
0	.07	.72	.08	1.69	3.18	9.73
15	.07	.67	.15	1.39	3.01	10.82
30	.08	.56	.36	1.33	2.72	11.50
60	.08	.41	.29	1.19	2.76	12.04
120	.09	.29	.64	1.29	2.73	14.98
240	.08	.48	.48	1.37	2.90	11.62
Second Cutting - Oats						
0	.05	.87	.10	1.48	2.55	4.22
15	.07	.68	.21	1.29	1.98	8.58
30	.08	.60	.35	1.25	2.05	11.58
60	.09	.38	.32	1.35	2.06	10.30
120	.09	.25	.58	1.21	2.08	10.49
240	.10	.41	.50	1.00	2.03	10.18
Only Cutting - Soybeans						
0	.09	1.26	.35	.73	1.41	8.75
15	.02	1.91	.53	1.05	3.68	1.65
30	.11	.98	.47	.58	1.23	10.99
60	.11	.90	.39	.61	1.31	12.63
120	.12	.64	.93	.61	1.26	11.35
240	.17	1.01	.76	.49	1.25	10.95

between 120 and 240 pounds per acre magnesium maximum growth was obtained and any magnesium above this concentration reduced the yield. The analysis of variance for the first cutting of oats is found in Table 19.

The increase in dry matter of the second cutting due to the addition of magnesium to the soil was very pronounced. All of the differences when compared to the no magnesium treatment were highly significant, as shown in Table 20. All of the additions of magnesium resulted in a greater than 100 per cent increase in yield. The highest yield in the second cutting was from the pots receiving the equivalent of 30 pounds per acre magnesium. Yields from the pots receiving more than 30 pounds per acre were not significantly different. It is interesting to note in Table 11 that the pots which received no magnesium produced more than twice as much dry matter in the first cutting as in the second cutting. The soil reserve of magnesium was depleted by the time of the first cutting to the extent that it became a limiting factor for plant growth thereafter. Also, seed contain a high concentration of magnesium and the plants were able to draw from the seed supply during the early stages of growth.

Seed yields were taken at the second cutting of oats. The increase due to the addition of magnesium was highly significant as shown in Table 21. Table 12 shows the yield increase as well as the number of seeds

TABLE 12

THE NUMBER AND WEIGHT OF OAT SEED FROM GREENHOUSE EXPERIMENT

Magnesium Applied Lbs./Acre	Number of Seed/Pot	Number of Seed/Plant	Number of Seed/Gram
0	27	.28	96
15	83	1.71	71
30	85	3.13	27
60	86	2.64	33
120	87	1.93	45
240	106	1.72	62

from each of the treatments that were required to weigh one gram. Plants receiving magnesium at the rate of 15 pounds per acre produced six times more seed than the plants receiving no magnesium while plants receiving the equivalent of 30 pounds per acre magnesium produced over 11 times more seed than the untreated plants. Probably equally important is the number of seed per gram resulting from the various magnesium treatments. All pots receiving magnesium produced about the same number of seed; however, the total weight of seed varied considerably. Ninety-six seed from the plants that received no magnesium weighed one gram, whereas it

took only 27 seed from the treatment equivalent to 30 pounds per acre magnesium to equal this weight. In addition to producing three hundred per cent more seed, the 30 pound per acre rate of magnesium increased the weight per seed more than three and one-half times as compared to seed produced where no magnesium was applied. Above the 30 pound per acre rate the total weight of seed produced by each application decreased and the number of seed per gram increased. Obviously, the seed harvested from the pots that received no magnesium were very light and of poor quality and while no germination tests were made it is reasonable to conclude that the percentage of seed germinating would be low.

Soybeans were planted immediately following the oats without any additional magnesium treatment to the soil. A complete nutrient solution was applied prior to planting. The highest yield of soybean plant material was from the pots that received the equivalent of 60 pounds per acre magnesium, Table 11. All magnesium treatments produced yields that were significantly greater than those obtained when no magnesium was applied, except where the 15 pounds per acre rate was added. At this rate the yield was significantly reduced as compared to the no magnesium treatment. The analysis of variance data are reported in Table 22. The cause of the reduced yield when 15 pounds per acre magnesium

was applied will be discussed under the paragraph heading, "Interactions." The largest yield increase in grams of plant material was about 44 per cent resulting from the addition of 60 pounds per acre magnesium. Magnesium when added in excess of this rate had a tendency to reduce the yield.

Interactions.--The results of the analyses of soil taken from the pots after the second cutting of oats and the soybean harvest are reported in Tables 13 and 14, respectively. Analysis of variance data for the magnesium concentration found at these samplings are reported in Tables 23 and 24. The magnesium found in the soil at the end of the oat experiment was directly proportional to the magnesium that was added. The total calcium and potassium values are about the same except where the equivalent of 15 pounds per acre of magnesium was added in which case they are higher.

Table 15 contains the pH values as well as the acid ammonium acetate extractable nutrients found in the soil after the termination of the soybean experiment. Acid ammonium acetate extracted less than one-half of the total magnesium at the lower magnesium concentrations and about 60 per cent of the total at the higher concentrations.

The pH values reported in Table 15 are the average of the three replications. The pH values do not differ

TABLE 13

ANALYSIS OF JONESVILLE FINE SAND FOR TOTAL MAGNESIUM, CALCIUM AND POTASSIUM FROM THE OATS EXPERIMENT IN THE GREENHOUSE

Magnesium Applied	Magnesium	Calcium	Potassium
(lbs./A.)	(lbs./A.)	(lbs./A.)	(lbs./A.)
0	85.0	400.0	146.0
15	95.0	461.0	164.3
30	115.0	389.0	176.0
60	135.0	367.0	185.0
120	185.0	298.0	185.3
240	305.0	379.0	187.3

TABLE 14

ANALYSIS OF JONESVILLE FINE SAND FOR TOTAL MAGNESIUM, CALCIUM AND POTASSIUM FROM THE SOYBEAN EXPERIMENT IN THE GREENHOUSE

Magnesium Applied	Magnesium	Calcium	Potassium
(lbs./A.)	(lbs./A.)	(lbs./A.)	(lbs./A.)
0	70.0	400.0	183.6
15	80.0	459.0	202.6
30	107.0	415.0	188.0
60	122.0	496.0	189.0
120	170.0	379.0	185.0
240	280.0	389.0	172.0

TABLE 15

ACID AMMONIUM ACETATE EXTRACTABLE NUTRIENTS FOUND IN THE SOIL AT END OF THE SOYBEAN EXPERIMENT

Magnesium Applied	pH	CaO	MgO	P_2O_5	K_2O
(lbs./A.)		(lbs./A.)	(lbs./A.)	(lbs./A.)	(lbs./A.)
0	5.26	247	34	6	26
15	4.96	322	42	9	45
30	5.17	238	65	8	32
60	5.16	247	79	7	33
120	5.06	242	165	8	24
240	5.25	238	254	8	21

greatly; however, the pH of the soil that received magnesium equivalent to 15 pounds per acre is the only one below pH 5.0. This is also the treatment that resulted in the exceedingly low yield mentioned previously. It is obvious that the pH 5.0 is very critical for this soil. The main reason why the plants did not grow was due to the lack of phosphorus. The lowest level of phosphorus in soybean plants reported in the literature was 0.09 per cent, according to Beason (14). The phosphorus found in the plants growing on the soils where the pH was below 5.0 was found to be 0.02 per cent as shown in Table 11. These plants contained higher concentrations of calcium, potassium, and nitrogen than any of the others. This is a clear indication that the plants were able to absorb the other ions but without adequate phosphorus were unable to use these nutrients. This soil was found to be unusually high in both iron and aluminum and the phosphorus is probably fixed as insoluble iron and aluminum phosphates. Mulder (109) stated that normal plant growth requires substantial amounts of magnesium and as the pH of the soil decreases the amount of available magnesium decreases. Also, the ability of the plant to absorb the magnesium decreases due to a limited root system. The failure of these plants to absorb phosphorus is probably due to a combination of the factors discussed above.

The magnesium uptake by oats and soybeans was proportional to that added to the soil until a certain concentration was reached as shown in Table 11. The analysis of variance for magnesium uptake gave "F" ratios that were significant at the one per cent level of probability as shown in Tables 25, 26 and 27. As the magnesium concentration is increased sufficiently over the other ions necessary for plant growth it may produce an antagonistic effect on certain of these ions.

The effect of soil applications of six levels of magnesium on the plant uptake of other ions is also presented in Table 11. The treatment mean squares and "F" ratios for these interactions are reported in Table 28.

As the magnesium level in the soil was increased the phosphorus uptake increased in direct proportion for all of the levels used in this experiment. The increase in phosphorus in the first cutting was not nearly so marked as in the second cutting of oats and in the soybean plant material. However, the uptake was significant at the five per cent level of probability. The phosphorus concentration in the second cutting was doubled and the magnesium concentration increased five fold by the addition of the equivalent of 240 pounds per acre magnesium. This difference was highly significant. The phosphorus

concentration of the soybean plants was almost doubled and the magnesium concentration more than doubled by the same concentration of added magnesium. These values were also highly significant.

The antagonistic effect of adding increasing concentrations of magnesium to the soil on calcium uptake by the plant was found to be highly significant. In the first cutting of oats the calcium level in plants harvested from soil that did not receive magnesium was found to be 0.72 per cent. As the rate of magnesium added to the soil was increased the calcium uptake decreased accordingly. Plants harvested from soil to which 120 pounds per acre of magnesium was applied contained as little as 0.29 per cent calcium. The highest rate of magnesium resulted in a lower yield and as the yield decreased the calcium content again increased. The second cutting repeated the same trend except the differences were larger resulting in significance at the higher probability level. The soybeans responded very much in the same manner except at the low pH values. The calcium requirement of soybeans was found to be greater than for the oats.

It is also evident from Table 11 that a definite optimum ratio of one per cent magnesium to two per cent calcium was necessary to give maximum forage yield. When the calcium was present in concentrations of three or

four times the magnesium concentration, reduced growth was noted.

Magnesium applied to the soil produced a highly significant reduction in the amount of potassium absorbed by oats and soybean plants. The depressing effect on potassium absorption was proportional to the magnesium added to the soil.

Magnesium when applied to the soil resulted in a significant depression in nitrogen uptake in the first cutting of oats. The same effect was noted in the second cutting even though the variation was such that it was not statistically significant. The "F" ratio did, however, approach significance at the five per cent level of probability.

Field.--The schedule of treatments in the field experiment was changed by eliminating the 15 pound per acre rate and adding the higher rate of 480 pounds per acre magnesium. The higher rate was used to insure adequate amounts of magnesium in case of heavy rainfall and also for the purpose of determining what was the highest rate that could be used in the field.

Yield.--Dolomite, a very insoluble calcium and magnesium compound when the pH increases to 5.7 or above, was one of the sources of magnesium used. The yield increased

as the amount of dolomite added to the soil increased to 240 pounds per acre, Table 16. When the rate of magnesium added to the soil was equivalent to 480 pounds per acre the yield was reduced as compared to the maximum yield obtained at the 240 pound per acre rate. The analysis of variance for the yield data is reported in Tables 29 and 30. Treatment, rate, and source x rate interactions were found to be highly significant. The addition of magnesium at rates equivalent to 240 pounds per acre in the form of dolomite resulted in a 60 per cent increase in yield of forage and a 64 per cent increase in seed when compared to plots receiving no magnesium.

It is obvious from the data presented in Table 17 that dolomite had no effect in changing the soil reaction even when applied at a rate in excess of two tons per acre. The insolubility of dolomite was also demonstrated by the failure of ammonium acetate to extract large amounts of calcium and magnesium. Plants harvested from plots that received increased amounts of dolomite failed to pick up magnesium in excess of that needed for growth. Soybeans growing on dolomite treated soil did not absorb appreciable amounts of magnesium except where the highest rate was added. The percentage magnesium found in plant material taken from plots that received the highest rate of magnesium in the form of dolomite was far below the optimum level of

TABLE 16

CHEMICAL COMPOSITION AND YIELDS OF SOYBEAN FORAGE FROM PLOTS RECEIVING SIX RATES OF MAGNESIUM FROM TWO SOURCES APPLIED TO UNIFORMLY FERTILIZED KLEJ FINE SAND[a]

Magnesium Source	Magnesium Applied	P	Ca	Mg	K	N	Yield	
							Seed	Dry Matter
	lbs./acre	(%)	(%)	(%)	(%)	(%)	bu/A	lbs/100'Row
Dolomite	0	0.27	1.04	0.36	1.65	2.66	5.3	2.40
	30	0.26	1.16	0.39	1.52	2.29	5.8	2.93
	60	0.25	1.07	0.39	1.60	2.53	6.8	3.17
	120	0.25	0.95	0.38	1.76	2.46	6.9	3.42
	240	0.24	0.88	0.39	1.56	2.30	8.2	3.98
	480	0.24	1.04	0.47	1.37	2.24	6.6	3.25
$MgSO_4$	0	0.24	1.12	0.33	1.70	2.28	5.5	2.51
	30	0.23	0.80	0.41	1.57	2.34	5.9	3.69
	60	0.22	0.87	0.60	1.53	2.37	7.8	3.66
	120	0.23	0.87	0.82	1.43	2.34	8.8	4.12
	240	0.24	0.68	0.95	1.46	2.50	4.4	3.28
	480	0.26	0.64	1.11	1.58	2.80	4.1	2.19

[a]Each value is the average of four replications.

TABLE 17

ACID AMMONIUM ACETATE EXTRACTABLE NUTRIENTS FOUND IN THE SOIL AT THE TERMINATION OF THE SOYBEAN EXPERIMENT

Magnesium Source	Mg. Rate Applied	pH	CaO	MgO	P_2O_5	K_2O
	lbs./A		lbs./A	lbs./A	lbs./A	lbs./A
Dolomite	0	5.96	567	51	26	65
	30	5.91	460	77	27	61
	60	6.06	613	80	22	53
	120	6.15	772	139	26	78
	240	6.08	628	179	25	57
	480	6.10	494	277	24	48
$MgSO_4$	0	5.86	437	29	23	55
	30	5.98	589	83	22	49
	60	6.10	580	107	23	52
	120	5.99	564	172	29	57
	240	5.89	470	215	21	57
	480	5.87	503	310	22	53

0.79 per cent reported by Beeson (14). The analysis of variance for magnesium uptake from the magnesium treated soil is shown in Table 31. The analysis of variance for the magnesium found in the soil at the termination of the experiment is in Table 32.

The same levels of magnesium when applied as magnesium sulfate produced effects that were quite different from those obtained from dolomite. The 30 pound per acre rate of magnesium as the sulfate produced almost as much dry matter as was produced when 240 pounds per acre of magnesium was added in the form of dolomite. The 60 pound per acre rate, in the form of magnesium sulfate, produced about as many seed as was produced on the plots that received 240 pounds per acre magnesium as dolomite. The maximum seed yield was produced when magnesium sulfate was applied at a rate equivalent to 120 pounds per acre magnesium. The highest seed yield from dolomite was obtained from plots that received the equivalent of 240 pounds per acre magnesium.

The magnesium content of the plant material harvested from the plots that received increased concentrations of magnesium sulfate emphasize the difference between the two sources. When magnesium sulfate was the source, significantly more magnesium was found in the plant material from plots receiving the 60 pounds per acre than from plots

receiving 480 pounds per acre magnesium in the form of dolomite. The magnesium content of the plant material did not increase to the optimum level of 0.79 per cent reported above until 120 pounds per acre of magnesium was applied to the soil in the form of magnesium sulfate. At this level of application the concentration was found to be 0.82 per cent and is very close to the reported optimum. This rate of magnesium was also the rate that produced the highest forage and seed yield. As the per cent magnesium increased above 0.82 per cent the yield of seed and plant material decreased rapidly. The plots that received the highest rate of magnesium in the form of magnesium sulfate produced less yield than where no magnesium was applied which indicated that the nutrient levels were badly out of balance.

The results of the analyses for total soil magnesium, calcium and potassium are reported in Table 18.

Interactions.--The interaction of the magnesium ion with the phosphate ion was found to exist much the same in the field as was found in the greenhouse when the source of magnesium was magnesium sulfate. The effect of adding magnesium, in the form of dolomite, to the soil at increasing levels was to reduce the phosphorus uptake by soybean plants. The reduction was not significant at the five per cent level of probability because of the variation between replications; however, the trend exists and if it is a

TABLE 18

TOTAL MAGNESIUM, POTASSIUM, AND CALCIUM FOUND IN KLEJ FINE SAND AT THE END OF THE SOYBEAN EXPERIMENT[a]

Magnesium Source	Magnesium Applied	Magnesium	Calcium	Potassium
	lbs./A.	lbs./A.	lbs./A.	lbs./A.
Dolomite	0	204	554	204
	30	212	548	190
	60	292	650	196
	120	376	892	210
	240	428	972	198
	480	576	1032	194
$MgSO_4$	0	174	514	196
	30	226	672	200
	60	240	672	196
	120	292	766	206
	240	280	558	196
	480	322	586	204

[a]Each entry is average of four replications.

true trend, it is an antagonistic effect produced by the phosphorus ion. There was a significant difference between the two sources as shown in Table 33.

The calcium uptake was depressed by the addition of increasing concentrations of magnesium to the soil. There was a general depressing effect due to magnesium when added in the dolomitic form as long as the yield was increasing. When the yield was decreased due to the addition of the highest concentration of magnesium, from dolomite, the calcium uptake increased.

Where magnesium was added in the form of magnesium sulfate, the uptake of calcium was depressed at all of the concentrations of magnesium used. The highest rate of magnesium added to the soil produced plants that contained only half as much calcium as the plants produced on plots receiving no magnesium. The treatment and source effects were highly significant as shown by Table 34. The rates were significant at the five per cent level of probability.

When magnesium was added to the soil it had a depressing effect on the potassium uptake by soybeans, especially when the source of magnesium was magnesium sulfate. The potassium concentration found in the plants did not decrease consistantly as the magnesium level of the soil was increased. The highest rate of magnesium in the form of dolomite reduced the potassium uptake significantly.

There was a variable effect of magnesium sources on the nitrogen content of the soybeans. When dolomite was the source, the nitrogen content in all of the plant material from magnesium treated plots was less than plant material from untreated plots. The reverse of this was true when magnesium sulfate was the source. As the rate of magnesium added to the soil in the form of magnesium sulfate was increased, the nitrogen content of the forage increased. The analysis of variance for the magnesium-nitrogen interaction is shown in Table 35.

SUMMARY AND CONCLUSIONS

An attempt was made to determine the effect ions present in soil and plant ash solutions have on the determination of magnesium using the flame spectrophotometer.

The ions that were under consideration for possible interferences were added in concentrations that would approximate their concentration in plant and soil ash solutions using several dilutions.

Of the three wavelengths studied, the 285.2 millimicron wavelength was far superior to either the 371.0 or the 383.0 millimicron wavelength with respect to the interference of extraneous ions. Both of the latter wavelengths were severely affected by the background produced by added ions. The determination of magnesium at either the 371.0 or 383.0 millimicron wavelength would be of limited value unless some method of removing this background effect could be devised. Since the 285.2 line was found to be free of background effect produced by added ions and superior to the other two wavelengths as far as other types of interferences were concerned it was selected as being the one most suitable for magnesium determinations in soils and plant materials.

Of all ions tested potassium, sodium, manganese, copper, nitrates, and zinc ions were the only ions without effect on the magnesium flame at any of the concentrations determined.

Several ions were found to produce interferences on the magnesium flame if present in sufficient concentrations. Iron was found to produce a depressing effect if in concentrations greater than 100 ppm. One gram plant samples ashed and diluted to 100 ml. volume would contain less than this concentration of iron. Iron is high in many soils and this concentration, or even greater, could be present in solutions of soil ash.

The calcium ion had a very slight enhancing effect on the magnesium flame which was directly proportional to the concentration of the calcium ion in solution. Concentrations up to 50 ppm calcium had no effect at the lower end of the curve; however, at the upper end it produced an enhancement of about one per cent. If magnesium was sufficiently high, calcium produced no effect until present in concentrations exceeding 200 ppm.

The chloride ion had no effect until it was added in excess of a one molar solution of hydrochloric acid. No soil or plant ash solutions would normally contain this much chlorine. If the ash is dissolved in hydrochloric acid the standards would also contain the same concentration of the acid, therefore, the chloride ion would be a constant

and would not cause trouble.

When the acetate ion was added there was no effect produced on the magnesium flame until the concentration of acetic acid was in excess of 0.2 molar. The acetate ion would not be present in sufficient concentrations in hydrochloric acid solutions of plant or soil ash to produce any effect.

Perchloric acid up to 4.0 molar concentration had no effect on the 100 ppm magnesium curve. When the 500 ppm magnesium curve was used it produced an enhancing effect. This ion could be a problem where wet ashing is used in total analysis; however, this effect could be diluted out or eliminated by using a lower magnesium standard curve.

The ions that were found to produce serious effects on the magnesium flame were sulfur, phosphorus, aluminum and silicon. Of the four mentioned, silicon was found to suppress the magnesium flame more than any of the other ions. The effect of silicon was eliminated by proper dehydration of the silica after ashing. If the silica has been properly dehydrated and the sample dissolved in dilute hydrochloric acid there will be only a trace of silica present since it is insoluble in acid solutions.

Aluminum was also found to produce a serious depressing effect on the magnesium flame which was in direct proportion to its concentration in solution.

The sulfur ion produced a very serious depressing effect on the magnesium flame emission which was greatest at the upper portion of the curve. A small amount of sulfur produced about the same amount of depression at the upper portion of the curve as a large amount produced at the lower end of the curve which indicated a chemical combination of the two ions had taken place.

The phosphorus ion like the sulfur ion produced a very marked depressing effect on the magnesium flame. The greatest effect was at the lower portion of the magnesium curve. The ions that were found to interfere most were ions that form compounds with high melting and boiling points with magnesium or the magnesium solvent.

Phosphorus and sulfur were the only ions present in sufficient quantities in plant ash solutions to cause a serious error. Since both of these are anions Dowex 1, an anion exchange resin, was used to separate these ions from magnesium. The resin was found to be very inefficient in removing phosphorus; however, it was very efficient in removing sulfur. The resin was found to remove phosphorus quantitatively provided the concentration entering the resin column did not exceed 17 ppm. There are several resins on the market that have a high capacity for phosphorus. The resin efficiency for phosphorus removal could have been increased by mixing one of the high

phosphorus capacity resins with Dowex 1 and using the mixture in each of the resin columns. One of the resins would function in removing the phosphorus and the other in removing the sulfur. This technique was not tried but is believed to have possibilities.

The flame method using the anion resin to separate the phosphorus and sulfur compared very favorably with the longer chemical method. The results were found to be about two and one-half per cent higher. The recovery of magnesium added to solutions of plant ash was very good at two different dilutions. In separating ions that produce serious effects on the magnesium flame the calcium values were increased over three fold when compared to the values obtained without the use of the resin. Since calcium was determined, a comparison of the flame method with the standard A.O.A.C. method was necessary to determine the reliability of the flame method. The calcium values using the resin to separate phosphorus and sulfur averaged about eight per cent higher than the same samples determined by the A.O.A.C. method. The eight per cent error can be attributed to enhancement due to other cations in the solution. The error appears large; however, when compared to the error that is present when the anions are not removed it represents a definite improvement in the flame method.

Iron and aluminum ions from the solution of soil ash had to be removed in the analysis of magnesium by the flame method because of their presence in high concentrations. A very simple procedure based on the A.O.A.C. method was used to precipitate these ions. By adjusting the pH of the soil solution to 6.5 using brome thymol blue indicator it was found that the precipitation of iron and aluminum was complete and that phosphorus was also precipitated at the same time. Three ions that caused the greatest amount of the interference were removed simultaneously with substantial increase in the calcium and magnesium concentrations found. Magnesium and calcium recoveries using this technique were very good. The flame method is a rapid method for the determination of magnesium and was found to be accurate if ions known to produce interferences were removed prior to the flame determination.

The greenhouse and field experiment, in addition to furnishing soil and plant material used in testing the method, produced interesting results.

These experiments indicated that where the soil is known to be low in magnesium, yields may be increased significantly by adding either dolomite or magnesium sulfate to the soil. Seed yields were increased even more than plant yields.

Dolomite was found to be very insoluble and consequently had not increased the pH of the soil significantly at the end of one year. The magnesium content of soybean plants was not significantly increased even when 480 pounds per acre of magnesium was added in the form of dolomite. The yields of plant material and beans were significantly increased.

Magnesium sulfate increased the yields of plant material and beans more than dolomite. Ninety pounds of magnesium in the form of magnesium sulfate produced as much as 240 pounds of magnesium applied as dolomite. In addition, it was found that the magnesium concentration in plants was doubled by the addition of 90 pounds per acre magnesium added as magnesium sulfate when compared to the 240 pound per acre rate using dolomite.

From the data obtained in the greenhouse and field experiments, in addition to applying dolomite periodically as determined by a soil test, a small amount of magnesium in a soluble form should be applied as a side dressing or incorporated into the fertilizer to be used on soils known to be deficient in this element.

The addition of magnesium to the soil was found to increase the uptake of phosphorus, the increase being in proportion to the amount of magnesium applied to the soil.

Magnesium applied to the soil significantly suppressed the uptake of calcium, potassium and nitrogen.

APPENDIX

TABLE 19

ANALYSIS OF VARIANCE FOR FIRST CUTTING OF OATS TAKEN FROM JONESVILLE FINE SAND IN THE GREENHOUSE

Source	d.f.	s.s.	m.s.	"F"
Total	17	84.5310		
Replications	2	9.8857	4.9428	
Treatment	5	46.6730	9.3346	3.34[a]
Error	10	27.9723	2.7972	

[a]Significant at the one per cent level of probability.

TABLE 20

ANALYSIS OF VARIANCE FOR SECOND CUTTING OF OATS TAKEN FROM JONESVILLE FINE SAND IN THE GREENHOUSE

Source	d.f.	s.s.	m.s.	"F"
Total	17	108.0779		
Replications	2	0.2839		
Treatment	5	103.8775	20.7755	530.39[a]
Error	10	3.9165	0.3917	

[a]Significant at the one per cent level of probability.

TABLE 21

ANALYSIS OF VARIANCE FOR OAT SEED YIELD TAKEN FROM JONESVILLE FINE SAND IN THE GREENHOUSE

Source	d.f.	s.s.	m.s.	"F"
Total	17	153,701.6120		
Replications	2	84.7780		
Treatment	5	142,310.2780	28,462.0560	25.17[a]
Error	10	11,306.5560	1,103.7000	

[a]Significant at the one per cent level of probability.

TABLE 22

ANALYSIS OF VARIANCE FOR SOYBEAN YIELD TAKEN FROM JONESVILLE FINE SAND IN THE GREENHOUSE

Source	d.f.	s.s.	m.s.	"F"
Total	17	241.4246		
Replications	2	.2220		
Treatments	5	238.7111	47.7422	175.91[a]
Error	10	2.7135	0.2714	

[a]Significant at the one per cent level of probability.

TABLE 23

ANALYSIS OF VARIANCE FOR TOTAL MAGNESIUM FOUND IN JONESVILLE FINE SAND AFTER THE OATS EXPERIMENT

Source	d.f.	s.s.	m.s.	"F"
Total	17	101,704.2778		
Replications	2	10.1110	5.0555	N.S.
Treatment	5	101,573.6110	20,314.7222	1,685.09[a]
Error	10	120.5558	12.0556	

[a]Significant at the one per cent level of probability.

TABLE 24

ANALYSIS OF VARIANCE FOR TOTAL MAGNESIUM FOUND IN JONESVILLE FINE SAND AFTER THE SOYBEAN EXPERIMENT

Source	d.f.	s.s.	m.s.	"F"
Total	17	401.2242		
Replications	2	.6109		
Treatment	5	332.2775	66.4555	27.31[a]
Error	10	24.3358	2.4336	

[a]Significant at the one per cent level of probability.

TABLE 25

ANALYSIS OF VARIANCE OF MAGNESIUM UPTAKE BY OATS FROM MAGNESIUM TREATED JONESVILLE FINE SAND

(First Cutting)

Source	d.f.	s.s.	m.s.	"F"
Total	17	0.6462		
Replications	2	0.0001		
Treatment	5	0.6458	0.1292	4,307[a]
Error	10	0.0003	0.0003	

[a]Significant at the one per cent level of probability.

TABLE 26

ANALYSIS OF VARIANCE OF MAGNESIUM UPTAKE BY OATS FROM MAGNESIUM TREATED JONESVILLE FINE SAND

(Second Cutting)

Source	d.f.	s.s.	m.s.	"F"
Total	17	0.4838		
Replications	2	0.0013	0.0007	
Treatment	5	0.4664	0.0933	58.31[a]
Error	10	0.0161	0.0016	

[a]Significant at the one percent level of probability.

TABLE 27

ANALYSIS OF VARIANCE OF MAGNESIUM UPTAKE BY SOYBEANS FROM MAGNESIUM TREATED JONESVILLE FINE SAND

Source	d.f.	s.s.	m.s.	"F"
Total	17	0.9009		
Replications	2	0.0369	0.0185	
Treatment	5	0.7729	0.1546	16.99[a]
Error	10	0.0911	0.0091	

[a]Significant at the one per cent level of probability.

TABLE 28

TREATMENT MEAN SQUARES AND "F" VALUES FOR MAGNESIUM INTERACTIONS

Crop	Interaction	Cutting	M.S.	"F"
Oats	Magnesium x Phosphorus	First	0.1023	5.41[a]
Oats	Magnesium x Phosphorus	Second	9.1556	12.68[b]
Soybeans	Magnesium x Phosphorus	Only	68.1333	30.51[b]
Oats	Magnesium x Calcium	First	0.1176	31.78[b]
Oats	Magnesium x Calcium	Second	0.1551	44.31[b]
Soybeans	Magnesium x Calcium	Only	0.5423	55.91[b]
Oats	Magnesium x Potassium	First	0.0861	19.57[b]
Oats	Magnesium x Potassium	Second	0.0757	7.42[b]
Soybeans	Magnesium x Potassium	Only	0.1152	22.15[b]
Oats	Magnesium x Nitrogen	First	0.0992	3.69[a]
Oats	Magnesium x Nitrogen	Second	0.1134	2.59
Soybeans	Magnesium x Nitrogen	Only	0.8649	455.21[b]

[a]Significant at the five per cent level of probability.
[b]Significant at the one per cent level of probability.

TABLE 29

ANALYSIS OF VARIANCE TABLE FOR SEED YIELD FROM SOYBEANS HARVESTED FROM KLEJ FINE SAND

Source	d.f.	s.s.	m.s.	"F"
Total	47	39,677.31		
Replications	3	100.00	33.63	N.S.
Treatments	11	32,392.56	2,944.78	135.27[a]
Source	1	1,073.52	1,073.52	4.93[a]
Rate	5	4,476.94	895.39	4.11[a]
S x R	5	26,842.10	5,368.42	24.66[a]
Error	33	7,183.86	217.69	

[a]Significant at one per cent level of probability.

TABLE 30

ANALYSIS OF VARIANCE TABLE FOR TOTAL YIELD OF SOYBEAN PLANTS HARVESTED FROM KLEJ FINE SAND

Source	d.f.	s.s.	m.s.	"F"
Total	47	37.33		
Replications	3	3.19	1.0633	4.70[a]
Treatments	11	26.68	2.4255	10.73[b]
Source	1	0.06	0.0600	
Rate	5	17.46	3.4920	15.44[b]
S x R	5	9.16	1.8320	8.10[b]
Error	33	7.46	0.2261	

[a]Significant at the five per cent level of probability.

[b]Significant at the one per cent level of probability.

TABLE 31

ANALYSIS OF VARIANCE TABLE FOR MAGNESIUM UPTAKE BY SOYBEANS

Source	d.f.	s.s.	m.s.	"F"
Total	47	3.1157		
Replications	3	0.0210	0.00700	9.46[a]
Treatments	11	3.0638	0.27850	296.31[a]
Source	1	1.1304	1.13040	1202.55[a]
Rate	5	1.1323	0.22646	240.91[a]
S x R	5	0.8011	0.16022	170.45[a]
Error	33	0.0309	0.00094	

[a]Significant at the one per cent level of probability.

TABLE 32

ANALYSIS OF VARIANCE ON TOTAL MAGNESIUM FOUND IN KLEJ FINE SAND AT END OF SOYBEAN EXPERIMENT

Source	d.f.	s.s.	m.s.	"F"
Total	47	200,109.00		
Replications	3	13,042.00	4,347.33	3.76[a]
Treatments	11	141,730.00	12,884.55	9.38[b]
Source	1	25,761.33	25,761.33	18.75[b]
Rate	5	92,774.75	18,554.95	13.51[b]
S x R	5	23,193.92	4,638.88	3.38[a]
Error	33	45,337.00	1,373.85	

[a]Significant at the five per cent level of probability.

[b]Significant at the one per cent level of probability.

TABLE 33

ANALYSIS OF VARIANCE TABLE FOR THE EFFECT OF MAGNESIUM ADDED TO KLEJ FINE SAND ON PHOSPHORUS UPTAKE BY SOYBEANS

Source	d.f.	s.s.	m.s.	"F"
Total	47	0.0338		
Replications	3	0.0055	0.0018	3.00[a]
Treatments	11	0.0086	0.0008	1.33
Source	1	0.0027	0.0027	4.50[a]
Rate	5	0.0025	0.0005	
S x R	5	0.0036	0.0007	1.17
Error	33	0.0197	0.0006	

[a]Significant at the five per cent level of probability.

TABLE 34

ANALYSIS OF VARIANCE TABLE FOR THE EFFECT OF MAGNESIUM ADDED TO KLEJ FINE SAND ON CALCIUM UPTAKE BY SOYBEANS

Source	d.f.	s.s.	m.s.	"F"
Total	47	2.7256		
Replications	3	0.2440	0.0813	
Treatments	11	1.2602	0.1146	3.10[a]
Source	1	0.4466	0.4466	12.07[a]
Rate	5	0.4741	0.0948	2.65[b]
S x R	5	0.3395	0.0679	
Error	33	1.2223	0.0370	

[a]Significant at the one per cent level of probability.
[b]Significant at the five per cent level of probability.

TABLE 35

ANALYSIS OF VARIANCE TABLE FOR THE EFFECT OF MAGNESIUM ADDED TO KLEJ FINE SAND ON NITROGEN UPTAKE BY SOYBEANS

Source	d.f.	s.s.	m.s.	"F"
Total	47	4.7277		
Replications	3	0.1562	0.0521	
Treatments	11	1.4249	0.1295	1.36 (2.08 for[a])
Source	1	0.0120	0.0120	
Rate	5	0.2435	0.0487	
S x R	5	1.1694	0.2339	2.45 (2.51 for[a])
Error	33	3.1466	0.0954	

[a]Significant at the five per cent level of probability.

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BIOGRAPHICAL ITEMS

Granville C. Horn was born September 28, 1926, at Gainesville, Florida. He attended Grammer School at the East Side Grammer School and was graduated from Gainesville High School June 12, 1944.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Agriculture and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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